Optimization of Nitrate Removal from Aqueous Solution by Amine-Functionalized MCM-41 using Response Surface Methodology

by

Lau Yoke Loon
16803

Dissertation submitted in partial fulfillment of
the requirement for
Bachelor of Engineering (Hons)
(Chemical Engineering)

SEPTEMBER 2015

Universiti Teknologi PETRONAS,
32610, Bandar Seri Iskandar,
Perak

CERTIFICATION OF APPROVAL

Optimization of Nitrate Removal from Aqueous Solution by Amine-Functionalized MCM-41 Using Response Surface Methodology

by

Lau Yoke Loon

16803

A project dissertation submitted to the

Chemical Engineering Programme

Universiti Teknologi PETRONAS

In partial fulfillment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

(CHEMICAL ENGINEERING)

Approved by,

_____

Dr. Yeong Yin Fong

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR, PERAK

September 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or person.

_____

LAU YOKE LOON

ABSTRACT

High concentration of nitrate in water may bring adverse effects to both health and environment such as blue baby syndrome and algal bloom. Among all the nitrate removal methods up to date, adsorption is more favourable due to its simplicity of design, economical operation and less sludge production. Amine functionalized mesoporous silica represents one of the potential adsorbents in nitrate removal process due to its high adsorption capacity. Also, previous study has shown that 20% loaded (AEPTMS) amine-functionalized MCM-41 could achieve high percentage of nitrate removal. However, optimization of experimental conditions such as initial nitrate concentration, weight of adsorbent and contact time of adsorbent is yet to be done. In this study, Response Surface Methodology (RSM) was used to optimize the experimental conditions in nitrate removal processes using 20% AEPTMS amine-functionalized MCM-41 as the adsorbent. The adsorbent was successfully synthesized using co-condensation method and then characterized by Fourier Transform Infrared Spectroscopy (FTIR) as well as Scanning Electron Microscope (SEM). Subsequently, total 19 experiments with different experimental conditions generated by the Design of Experiment (DoE) software has been successfully carried out. From the experimental result, a quadratic model was used to fit the experimental data. The ANOVA analysis showed that the model was significant with R^2 of 0.9935. The interaction between the three variables was then demonstrated in three-dimensional surface plot through prediction from the model. It was found that the highest percentage removal of nitrate was 70% obtained using initial nitrate concentration of 0.25 mM, weight of absorbent of 0.50 g and contact time of 1 h. Meanwhile, the optimum percentage nitrate removal of 56% was obtained at the optimum conditions with initial nitrate concentration of 0.25 mM, weight of adsorbent of 0.124 g, and contact time of 1 h. Lastly, the adsorption isotherm study was carried out and Freundlich isotherms was found to fit the adsorption data better compared to Langmuir isotherms.

ACKNOWLEDGEMENTS

First and foremost, I would like to thank Universiti Teknologi Petronas (UTP) for giving me this opportunity to conduct my Final Year Project (FYP). Indeed, UTP has many high technology equipment and devices which enhances the learning process of students.

Besides, I would like to express my greatest appreciation to my supervisor, Dr. Yeong Yin Fong for her supervision, guidance and encouragement throughout the entire project. She is very knowledgeable, patient and experienced in chemical engineering department. I was indeed very lucky to be placed under her supervision. Upon the completion of this project, I have learnt a lot of new things especially regarding the field of my project.

Next, I would also like to thank the PhD student, Lai Li Sze, who has been helping me to analyse the experiment results. She is also quite experienced in the particular field and always patient in explaining things to me.

Moreover, I must also thank all the technicians who have been helping me to run the sample test as well as guiding me to use the equipment. I have learned quite a lot from them as well.

In short, without the help and guidance from all the parties involved above, my final year project will not be completed successfully. Hence, I would like to say a million thanks to those who have helped and guided me all this while.

TABLE OF CONTENTS

CERTIFICATION OF APPROVAL ii
CERTIFICATION OF ORIGINALITY iii
ABSTRACT iv
ACKNOWLEDGEMENTS v

CHAPTER 1: INTRODUCTION 1
1.1 Background of Study 1
1.2 Problem Statement 2
1.3 Objective 3
1.4 Scope of Study 3
1.5 Relevancy of Project 4

CHAPTER 2: LITERATURE REVIEW 5
2.1 Effects of Nitrate 5
2.2 Existing method in Nitrate Removal 6
2.3 Mobil Crystalline Materials (MCM) 9
2.4 Amine functionalized MCM-41 10
2.5 Response Surface Metholodogy (RSM) 11

CHAPTER 3: METHODOLOGY 12
3.1 Project Methodology 12
3.2 Response Surface Methodology (RSM) 13
3.2.1 Identify operating parameters and their ranges 13
3.2.2 Design of Experiments 14
3.3 Synthesis of 20% loaded AEPTMS-MCM 41 adsorbent 19
3.4 Characterization 20
3.4.1 Fourier Transform Infrared Spectroscopy (FTIR) *[Model: Shimadzu 8400s]* 20
3.4.2 Scanning Electron Microscope (SEM) *[Model: Hitachi TM 3030]* 20

3.4.3 UV-Vis Spectroscopy *[Model: Cary 60]* 20
3.5 Nitrate Removal Test.....21
3.5.1 Adsorption Study.....21
3.5.2 Adsorption Isotherms Study.....22
3.6 Equipment and Chemicals Used.....23
3.6.1 Equipment and Apparatus 23
3.6.2 Chemicals 23
3.6.3 Software.....23
3.7 Milestones 24
3.8 Activities Gantt Chart.....25

CHAPTER 4: RESULTS AND DISCUSSION 27
4.1 Characterization.....27
4.1.1 Fourier Transform Infrared Spectroscopy (FTIR).....27
4.1.2 Scanning Electron Microscope (SEM).....28
4.2 Nitrate Removal Study 29
4.2.1 Statistical Model Analysis.....29
4.2.2 Optimization.....36
4.2.3 Adsorption Isotherms Study.....38

CHAPTER 5: CONCLUSION & RECOMMENDATIONS 43
5.1 Conclusion.....43
5.2 Recommendation.....45

REFERENCES.....46
APPENDICES 52

LIST OF FIGURES

FIGURE 1.	Pore system of MCM-41 and MCM-48 [44]	9
FIGURE 2.	Research activities of this project	12
FIGURE 3.	Response Surface Design in DoE	14
FIGURE 4.	Input data of manipulated variables	15
FIGURE 5.	Input data of response variables	15
FIGURE 6.	Experiment runs generated by Design Expert Software	16
FIGURE 7.	FTIR Spectra for 20% AEPTMS amine-functionalized MCM-41 adsorbent	27
FIGURE 8.	SEM images of 20% AEPTMS amine-functionalized MCM-41 a) Magnification: x2.0k and b) Magnification: x4.0k	28
FIGURE 9.	Predicted versus Actual Design Expert Plot	31
FIGURE 10.	Percentage of Nitrate Removal against Weight of Adsorbent and Initial Nitrate Concentration at Contact time of 12.5 h	33
FIGURE 11.	Percentage of Nitrate Removal against Contact Time of Adsorbent and Initial Nitrate Concentration at Weight of Adsorbent of 0.275 g	34
FIGURE 12.	Percentage of Nitrate Removal against Contact Time of Adsorbent and Weight of Adsorbent at Initial Nitrate Concentration of 0.15 mM	35
FIGURE 13.	Langmuir isotherm plots for nitrate adsorption by 20% AEPTMS amine-functionalized MCM-41with different adsorbent dosage: (a) 0.050 g (b) 0.275 g (c) 0.500 g	39
FIGURE 14.	Freundlich isotherm plots for nitrate adsorption by 20% AEPTMS amine-functionalized MCM-41with different adsorbent dosage: (a) 0.050 g (b) 0.275 g and (c) 0.500 g	41

LIST OF TABLES

TABLE 1.	Adsorption capacities for different type of adsorbents [6]	8
TABLE 2.	Range of experimental parameters used in nitrate adsorption process	13
TABLE 3.	Amount of reactants required for the synthesis of 20% loaded AEPTMS MCM-41	19
TABLE 4.	FYP I and II Key Milestones	24
TABLE 5.	FYP I Gantt Chart	25
TABLE 6.	FYP II Gantt Chart	26
TABLE 7.	Nitrate Removal Experiment Runs and Responses	29
TABLE 8.	ANOVA results for the models evaluation	30
TABLE 9.	Optimization goal for different criteria in nitrate removal study	36
TABLE 10.	Optimum conditions generated by DoE for nitrate removal process using 20% AEPTMS amine-functionalized MCM-41.	37
TABLE 11.	Experiment verification for optimum conditions in nitrate removal process	37
TABLE 12.	Langmuir parameters of studied samples	40
TABLE 13.	Freundlich parameters of the studied sample at different adsorbent dosage	42

CHAPTER 1
INTRODUCTION

1.1 Background of Study

Nitrate is widely used to produce fertilizer due to its high solubility and biodegradability in water. However, the excessive use of fertilizer in agriculture has caused leaching of nitrate to the ground water, which then contaminates the river around the agricultural area and water supply [1, 2]. High nitrate concentration in drinking water may bring us various health effects. For instance, infants under six months fed with nitrate contaminated water could have methemogloinemia or blue baby syndrome, and if untreated, may die [3, 4]. Therefore, it is essential to remove nitrate from our water supply.

Various methods have been developed for nitrate removal up to date. The most common methods are ion exchange, reverse osmosis and electrodialysis [5-7]. Even though these methods have their own advantages in removing nitrate, but still they possess some major drawbacks such as high waste disposal, formation of disinfection by-products, expensive and operation complexity [6, 8]. Adsorption, on the other hand, is more favourable for nitrate removal process due to its simplicity of design, ease of operation, convenience and less to no waste disposal [7, 9]. Compared to the other methods that pose disposal problem, adsorption is considered a more environmental friendly and effective approach.

Among all the conventional adsorbents, mesoporous materials are most popular due to its excellent performance in adsorption processes. Generally, mesoporous materials have large surface area, high pore volume, high thermal stability, and suitable for surface modification [9-11]. These materials are normally functionalized in order to further

improve their adsorption capacities [11, 12]. According to the preliminary study, MCM-41 grafted with 20% AEPTMS could achieve high percentage of nitrate removal [13]. However, optimization of the operating parameters in nitrate adsorption process are yet to be done. Hence, in this work, Response Surface Methodology (RSM) will be used to find the optimum parameters in nitrate adsorption process in order to further increase the adsorption efficiency.

Response Surface Methodology (RSM) is the most widely used analytical tool in any optimization processes. It is used for designing experiments, constructing experimental models, evaluating the effects of parameters simultaneously and searching for the optimum conditions to achieve the desired response [14, 15]. Compared to one variable at a time (OVAT) which could not investigate the effects between several variables and requires large number of experimental runs, RSM is more commonly used as it could simultaneously optimize several variables at a time and thus reduce the number of experimental trials [16-19]. It is less time-consuming and requires less materials for the experiment. Since optimization of nitrate removal process involves several parameters that are dependent on each other and the range of parameters is big, RSM is more suitable to be used as the optimization tool to find the optimum parameters for desirable response.

1.2 Problem Statement

In the previous study [13], even though the newly developed adsorbent, AEPTMS (3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane) loaded MCM-41 had achieved high percentage of nitrate removal up to 80%, the optimization of experimental parameters such as initial nitrate concentration, contact time of adsorbent, weight of adsorbent as well as the interaction between these parameters are yet to be studied. Optimization of these parameters is important to further improve the adsorption efficiency. It is believed that after the optimization study, the percentage of nitrate removal can be maximized by using the optimal values of experimental conditions. By then, the adsorbent (AEPTMS loaded MCM-41) developed previously will be used for nitrate removal process.

1.3 Objective

The objectives of this project are:

1. To synthesize 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (AEPTMS) functionalized MCM-41 adsorbents through co-condensation method.
2. To characterize the structural properties of the resultant adsorbent using different analytical tools such as Fourier Transform Infrared Spectroscopy (FTIR) and scanning electron microscope (SEM).
3. To optimize the experimental parameters in nitrate adsorption process including initial nitrate concentration, contact time of adsorbent and weight of adsorbent using Response Surface Methodology (RSM).
4. To study the nitrate adsorption behavior of the synthesized adsorbents by conducting kinetic and isotherms studies.

1.4 Scope of Study

The scope of study in this research involves the optimization of crucial parameters in nitrate adsorption process. Three parameters including initial nitrate concentration, contact time of adsorbents and weight of adsorbents will be identified to be the main parameters in the adsorption process. In this project, Design of Experiment (DoE) is used as the optimization tool as it can reduce the total number of experimental runs and it is more cost-effective. First, the DoE software, Design Expert version 6.0.6 will be used to construct the model and generate a number of experimental runs. Then, the experiments were conducted to collect the data for response variable. The experiments involve the synthesis of AEPTMS MCM-41 adsorbents as well as the characterization of the synthesized adsorbents using Fourier Transform Infrared Spectroscopy (FTIR) and scanning electron microscope (SEM). After the adsorbents have been synthesized and characterized, nitrate removal study were carried out based on the experiment condition suggested by Design Expert. Subsequently, kinetics and isotherms studies were also conducted to study the nitrate adsorption behavior. After all the experiments have been

done, Design Expert was again used to evaluate and optimize the model. The accuracy and validity of the model will be verified using analysis tool such as Design-Expert plot. Finally, optimization will be performed using Design Expert to find out the optimum parameters in nitrate adsorption process.

1.5 Relevancy of Project

The contamination of nitrate in drinking water has been a very serious issue since last few decades due to its impact on human health and environment. Hence, this project is considered important and relevant as it involves the development of new technology to remove nitrate from aqueous solution. Even though adsorption is widely used in nitrate removal process, optimization of operating parameters is rarely conducted. In this project, the adsorbent synthesized in the preliminary study is used for the nitrate removal process but the operating parameters are optimized by using Response Surface Methodology (RSM) to further improve its adsorption efficiency. It is believed that this project can maximize the adsorption efficiency of the adsorbent by optimizing the operating parameters such as initial nitrate concentration, contact time of adsorbents and mass of adsorbent.

1.6 Feasibility of Project

This project is feasible as the time frame given is sufficient (7 months) and the methodology used is not time consuming. The equipment and materials are all readily available in the laboratory. Besides, the use of Response Surface Methodology (RSM) makes the project become more systematic and less time consuming by reducing the number of experimental runs.

CHAPTER 2
LITERATURE REVIEW

2.1 Effects of Nitrate

Nitrate which can be expressed as NO_3 are found naturally on Earth. Natural reaction of nitrogen in atmosphere with rain water forms nitrate and ammonium ions [20]. Other than that, nitrates can also be found in the food that we may consume in our daily life. For instance, they are found naturally in vegetables and added to various meat products as preservative [21]. Nitrates is a dietary requirement to all organisms. In moderate amount, nitrates are considered harmless to our health and the ecosystems [22].

Nitrate is an odourless, colourless and tasteless compound [23]. It is highly soluble in standard temperature and pressure. Due to its high solubility and biodegradability, nitrates are used to produce fertilizers in agriculture. The most common nitrogen fertilizers are ammonium nitrate (NH_4NO_3) and sodium nitrate ($NaNO_3$) [24]. Generally, the concentration of nitrate in ground water is low. However, the leaching of nitrate from the excessive use of fertilizers as well as the uncontrolled land discharges of treated waste water contaminates the ground water and drinking water, which then leads to eutrophication [7, 25-27]. According to study by researchers at UC Davis, approximately 10 percent of the 2.6 million residents in Salinas Valley and Tulare Lake Basin, United States might be drinking nitrate-contaminated water [28]. If nothing is to be done, the number of affected residents may reach 80 percent by 2050. On the other hand, eutrophication can also cause huge dead zones in coastal ecosystems, where algal blooms deplete oxygen. One of the dead zones can be found in the Gulf of Mexico, which is roughly the size of New Jersey [26].

From both of the cases above, it is shown that intensive agricultural areas have high level of nitrate concentration due to the use of fertilizers. When the nitrate concentration in the ground water above the safe levels proposed by EPA, it can pose a threat to human health. The maximum contaminant level (MCL) of nitrate set by EPA is 10 mg/L of NO_3-N or 45 mg/L of NO_3 [22]. Among the health effects caused by nitrate contaminated water are hair loss, skin rashes, birth defects and also "blue baby syndrome" [22, 25, 28]. Infants below six months with blue baby syndrome will become seriously ill, experience shortness of breath and if untreated, will die [29].

2.2 Existing method in Nitrate Removal

The high stability and solubility of nitrate ion makes it difficult to be removed by conventional water treatment process such as coagulation, precipitation and filtration [6]. Up until today, various methods and technologies have been researched and applied to remove nitrate from waste water. Among the conventional methods for nitrate removal are chemical processes (selective ion exchange, breakpoint chlorination, chemical coagulation), biological processes (denitrification, nitrification, oxidation ponds, harvesting of algae), physical operation (ammonia stripping, electrodialysis, reverse osmosis) and land application (overland flow, irrigation rapid infiltration) [5, 27, 30].

Denitrification is commonly employed in water treatment processes for nitrate removal. There are two types of denitrification, namely biological denitrification and chemical denitrification [8]. Biological denitrification is a process where certain bacteria use nitrate as terminal electron acceptor for their anaerobic respiration in the absence of oxygen and thus reduce the nitrate ion to nitrogen through the following sequence [31]:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO\ (g) \rightarrow N_2O\ (g) \rightarrow NO\ (g)$$

According to findings, enhanced biological denitrification in cyclic rotating bed reactor with catechol as carbon source could achieve up to 95% of nitrate removal at an inlet concentration of 1000 mg NO_3^-/L [32]. However, the significant drawbacks of nitrate

removal using biological denitrification include slow start up, high complexity, necessity of continuous operation, requires post treatment, and possible sensitivity to environment [6].

Chemical denitrification, on the other hand, uses metal such as palladium, platinum, copper and tin to reduce nitrate to other forms. However, this process normally require a low pH and needs addition of hydrogen gas or other strong reductants to achieve better performance [8]. In contrast to biological denitrification, the percentage of nitrate removal using this method is lower. According to one of the researches, chemical dentrification using zero-valent magnesium powder could only achieve total nitrogen removal of 70% under ambient temperature and pressure [33].

Besides denitrification, the alternative methods used for nitrate treatment are ion exchange, reverse osmosis, and adsorption [6, 30]. The most commonly used method is ion exchange due to its simplicity, effectiveness and lower initial cost [34]. Ion exchange involves the binding of nitrate ions to an ion exchange resin and at the same time displace the chloride ions. The resin is periodically regenerated with a concentrated salt solution [6]. In ion exchange, the nitrate removal efficiency can be as high as 96% [30]. However, its primary disadvantage includes brine waste disposal and potential for formation of disinfection by-product such as nitrosamine. Nitrosamine are potential carcinogens in drinking water at low part-per-trillion levels [8].

On the other hand, reverse osmosis is normally used to treat multiple contaminants simultaneously. This includes ions and metals (nitrate, sodium, potassium, aluminium), particles, pesticides as well as radionuclides (radium, uranium) [35]. Reverse osmosis removes large number of contaminants from water by pushing the water under pressure through a semi-permeable membrane [30, 36]. In reverse osmosis, 91.3% to 99.8% of the contaminants such as metal elements, organic and inorganic compounds can be removed [37]. However, the main disadvantages of reverse osmosis are high operating cost, high energy demands, membrane fouling, waste disposal and operation complexity [6].

Among all the conventional methods in nitrate removal, adsorption is believed to be the most promising methods due to its simplicity of design, ease of operation, convenience and less to no waste disposal [7, 9]. Generally, adsorption involves the process of removing a soluble substance from water using an adsorbent. Among the adsorbents that have been used to remove nitrate so far are carbon-based sorbents, agricultural wastes sorbents, industrial wastes sorbents, biosorbents and miscellaneous adsorbents [7]. The adsorption capacities of each types of adsorbents is tabulated in TABLE 1.

Even though there are many adsorbents developed up to date, but most of them have poor selectivity, limited surface area and insufficient adsorption capacities [38]. Mesoporous silica, under the category of miscellaneous adsorbents has recently attracted the interest of researchers. This type of material has high surface area, high pore volume and appropriate surface for functionalization [10, 11, 39]. It is also proven that it has high adsorption capacity for nitrate ions in water (46.5 mg NO_3^-/g) [9].

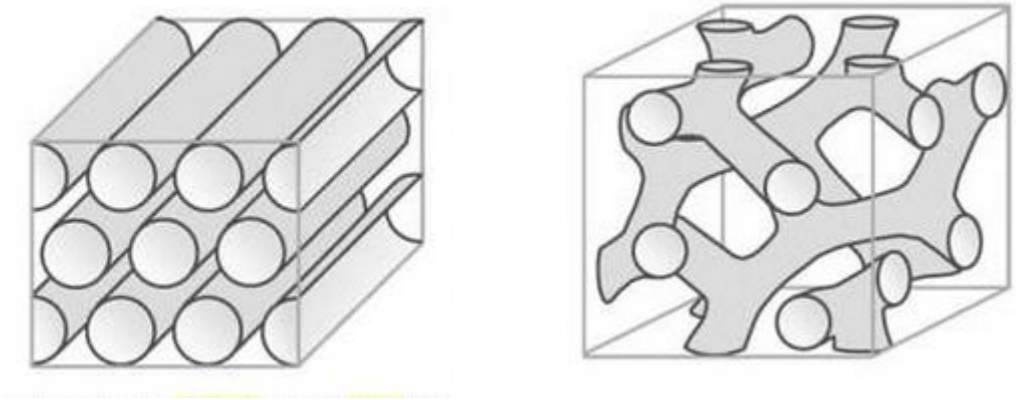
TABLE 1. Adsorption capacities for different type of adsorbents [6]

Type	**Adsorbents**	**Adsorption Capacity**
Agricultural waste sorbents	Sugarcane bagasse	1.41 mmol/g
	Raw wheat residue	0.02 mmol/g
	Rice Hull	1.32 mmol/g
Biosorbents	Bamboo charcoal	0.10 mmol/g
	Chinese reed	7.55 mg/g
	Chitosan beads	90.7 mg/g
Carbon-based sorbents	Carbon nanotubes	25 mmol/g
	H_2SO_4 treated carbon cloth	2.03 mmol/g
	Powdered activated carbon	10 mmol/g
Industrial waste sorbents	Original red mud	1.859 mmol/g
	Activated red mud	5.858 mmol/g
Natural sorbents	Modified bentonite	12.83 – 14.76 mg/g
	Modified zeolite	0.6 – 0.74 mmol/g
	Surfactant-modified sepiolite	0.45 mmol/g
Miscellaneous adsorbents	Ammonium-functionalized mesostructured silica	46.0 mg/g
	Layered double hydroxides	20–35 mg/g
	Nano-alumina	4.0 mg/g

2.3 Mobil Crystalline Materials (MCM)

Recent development of nanotechnology and mesoporous silica materials have gained interest of researchers all over the world due to the various promising advantages that these materials can provide. Typical mesoporous silica materials have large surface area, high pore volume, well-ordered and uniform pore with adjustable pore size ranged from 2 to 50 nm [10, 11, 40]. These features and characteristics make them very useful for wide variety of applications such as catalysis, adsorption, separation, biosensor, drug delivery and imaging [41, 42].

MCM (Mobile Crystalline Materials) is a series of mesoporous materials that were first synthesized by Mobil's researchers in 1992. MCM has pore diameter ranged from approximately 2 to 10 nm [43]. The most common types of MCM are MCM-41 and MCM-48. MCM-41 has a hexagonal array of unidirectional pores whereas MCM-48 has a cubic pore system as shown in FIGURE 1 [44]. Among the mesoporous materials, MCM-41 is most keenly researched by researchers due to its high specific surface area ($1000 m^2/g$), uniformity of pores, narrow pore distribution, regulated pore diameter and high thermal stability [39]. In this research, MCM-41 will used as the adsorbent and it will be functionalized to increase its adsorption capacity for nitrate removal process.



MCM 41 MCM 48

FIGURE 1. Pore system of MCM-41 and MCM-48 [44]

2.4 Amine functionalized MCM-41

Functionalization involves the process of adding new features, functions, properties or capabilities to certain material by changing the surface chemistry of the material. The most common examples of functionalization include water-repellent coatings for automobile windshields and hydrophilic coatings for contact lenses [45].

In adsorption process, mesoporous materials such as MCM-41 and MCM-48 are also functionalized to improve their adsorption capacities. Generally, these mesoporous materials have insufficient catalytic active sites and metal ions to be adsorptive and thus functionalization of these materials is crucial [46]. In one of the researches, the effect of grafted amine group on the adsorption of CO_2 in MCM-41 was investigated. From the result, it is proven that the CO_2 adsorption capacity increased with the increasing number of amine groups grafted [47]. On the other hand, ammonium grafted MCM-48 has also shown a greater performance in the removal of nitrate and phosphate ions at high concentrations compared to the pure MCM-48 [38].

Generally, there are two ways to carry out functionalization, namely post-grafting and co-condensation [10, 11, 38]. In post-grafting method, the functional molecules are grafted only on the external surface and near to the pores entrance [48]. While in co-condensation method, synthesis and functionalization of silica is done with one-step reaction with organic groups uniformly distributed on both inside of the pores and surface of the pores [10]. The post-grafting method is relatively convenient and simple compared to co-condensation method. However, it has several shortcomings such as reducing pore size, pore blocking at the aperture, difficulty in controlling the loadings as well as nonhomogeneous distributions of organic groups in the mesopores [11, 49]. All these shortcomings can be avoided by using co-condensation [49].

Hence, in this work, functionalization of MCM-41 using tertiary amine source (AEPTMS) will be done via co-condensation. AEPTMS is used for the functionalization as it could provide good result in nitrate removal process. According to the preliminary

study, 20% loaded AEPTMS MCM-41 could achieve up to 80% of nitrate removal from aqueous solution [13].

2.5 Response Surface Metholodogy (RSM)

Even though the preliminary study has proven that 20% loaded AEPTMS MCM-41 could achieve high percentage of nitrate removal, but the optimum experimental parameters such as initial nitrate concentration, contact time of adsorbent, weight of adsorbents are yet to be determined. Optimization of these parameters are essential as it can further improve the adsorption efficiency of nitrate removal process.

Traditionally, one variable at a time (OVAT) is used to perform optimization. It varies one factor or variable at a time while keeping others fixed [50]. This particular variable is changed until optimum result is achieved. Then, the same thing is repeated for second, variable, third variable and so on. The major drawback for this optimization method is that it fails to represent the effects of interaction between different factors [17]. Besides, it also increases the number of experiments necessary to carry out the research, which then leads to high time consumption, high expenses as well as high consumption of reagent and material [16, 51].

In order to overcome these shortcomings, response surface methodology (RSM) is used. RSM is a collection of mathematical and statistical method based on the fit of a polynomial equation to the experimental data [16]. It is used for designing experiments, building and analyzing models, evaluating simultaneous effects of several variables and eventually searching optimum conditions for desirable responses [14, 18]. Compared to OVAT, RSM is not only able to simultaneously optimize multiple variables at a time to achieve desired response, but also able to reduce number of experiments needed to be carried out [18, 19]. Therefore, in this work, response surface methodology (RSM) will be used as an optimization tool to optimize the experimental parameters for nitrate removal process using AEPTMS MCM-41 as the adsorbent.

CHAPTER 3
METHODOLOGY

3.1 Project Methodology

FIGURE 2 shows the research activities of this project. The detail elaboration of each of the activities will be included in the following sections.

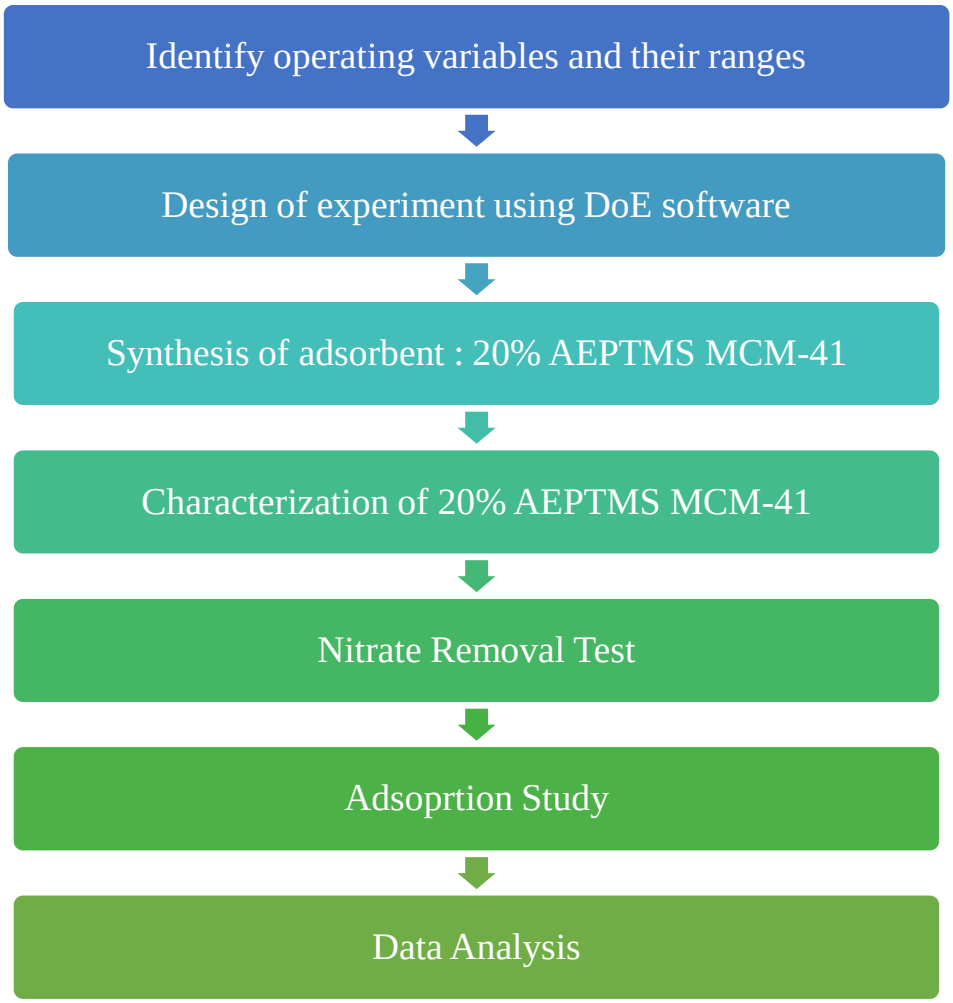


FIGURE 2: Research activities of this project

3.2 Response Surface Methodology (RSM)

3.2.1 Identify operating parameters and their ranges

In order to maximize the adsorption efficiency of nitrate removal process, the main factors that can affect the process must be verified first. Among the most common parameters that will affect the adsorption efficiency in nitrate removal process are initial concentration of nitrate, contact time of adsorbents and weight of adsorbents. Therefore in this project, the optimum values for these three parameters was determined by using Response Surface Methodology (RSM). According to the literature, the initial nitrate concentration used for nitrate adsorption study is normally ranged from 0.16 mM to 1.61 mM while the weight of adsorbents used is ranging from 0.05 g to 0.50 g [5, 25, 52, 53]. On the other hand, the contact time of adsorbents is ranged from 1 hour to 24 hours [25, 52, 54, 55]. Based on the above analysis, a suitable range for the respective parameters is identified and set as shown in TABLE 2.

TABLE 2. Range of experimental parameters used in nitrate adsorption process

No.	Experimental Parameters	Range of Parameters
1	Initial nitrate concentration	0.05 mM – 0.25 mM
2	Weight of adsorbents	0.05 g – 0.50 g
3	Contact time of adsorbents	1 hour – 24 hours

3.2.2 Design of Experiments

In the present work, the software Design Expert version 6.0.6 was used to design the experiment using Response Surface Methodology (RSM). This software offers a wide range of designs which can handle both response variable like percentage of nitrate removal and manipulated variables such as contact time of adsorbents and weight of adsorbents. Through the result and analysis from the software, the optimum values for the variables contributed to highest percentage of nitrate removal could be obtained.
There were three major steps in designing the experiment [56]:

Constructing the design

This step involved input of information needed to construct the design. For instance, name and ranges of variables as well as degree of replication. The steps in constructing the design are as follows:

1. Choose design method: RSM → CCD

   Standard RSM design called Central Composite Design was chosen to generate the experimental design for nitrate removal process. FIGURE 3 shows the display of Response Surface design in Design Expert. The numeric factors refer to the total number of parameters or variables, which in this case is three. The categorical factor was set as default.

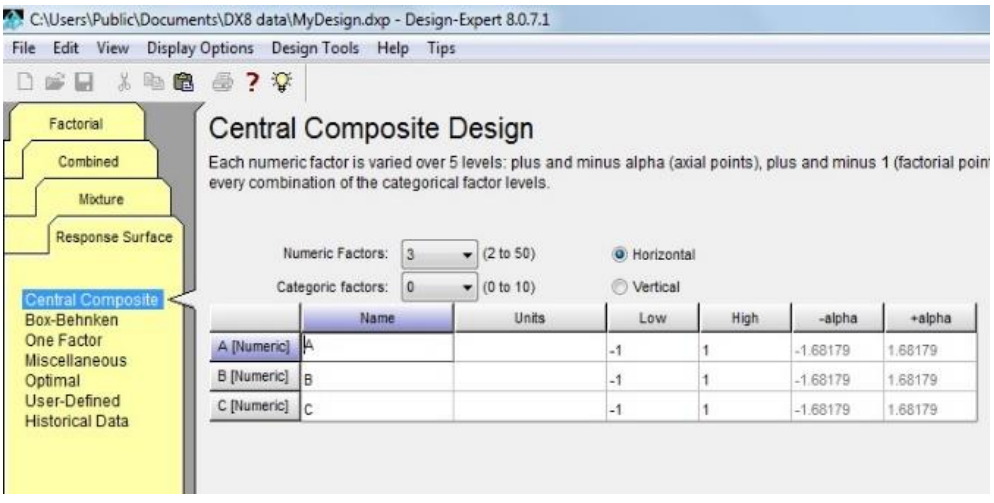


FIGURE 3. Response Surface Design in DoE

2. Input data for variables and response

FIGURE 4 shows the input data entry in Central Composite Design (CCD) window. The input data name for A, B and C was initial nitrate concentration, weight of adsorbents and contact time of adsorbent respectively. The “Low” and “High” column represents the range of parameters, which in this case the values in TABLE 2 were key in.

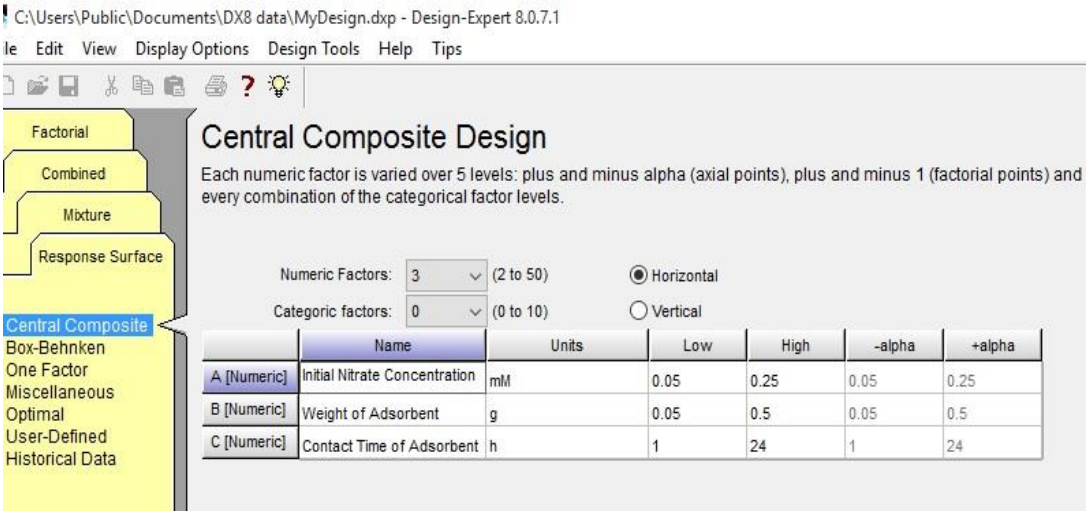


FIGURE 4. Input data of manipulated variables

On the other hand, FIGURE 5 shows the input data for response variable. The response variable for this experiment was percentage of nitrate removal and the unit was in %.

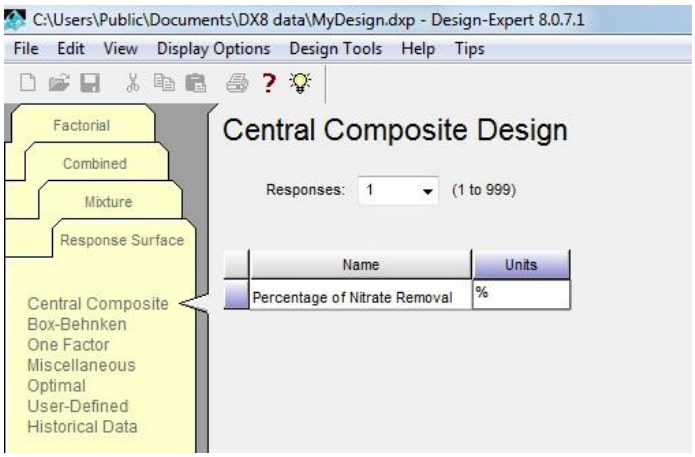
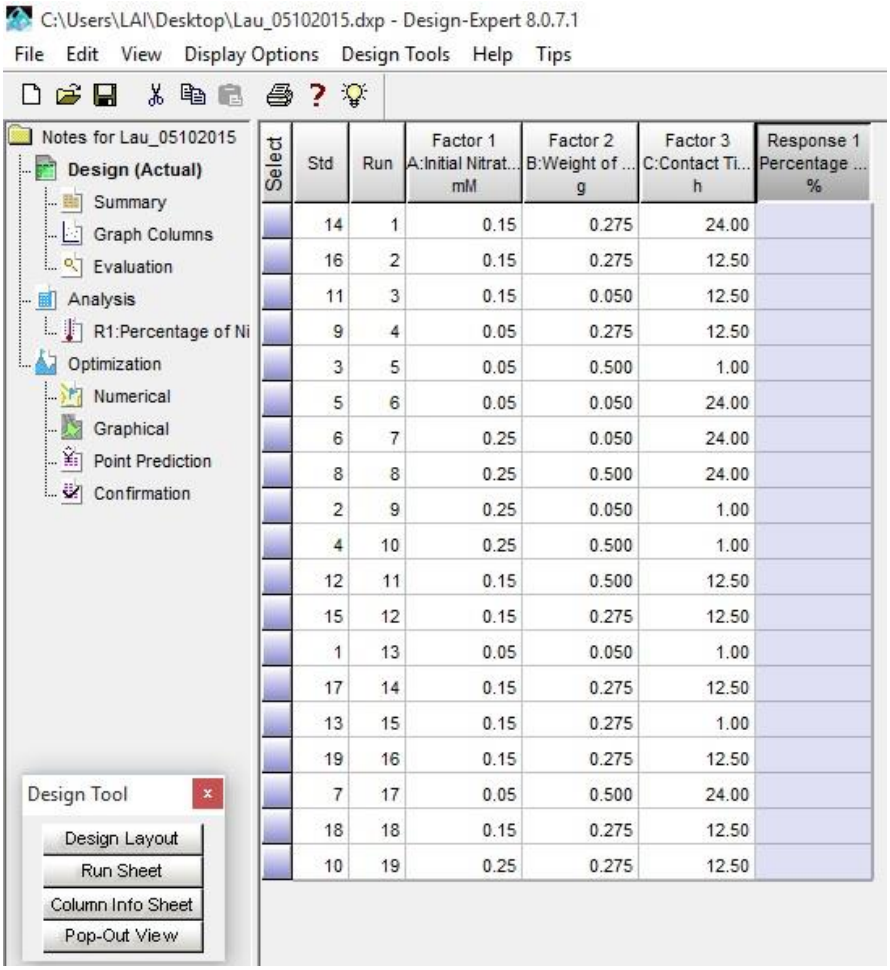


FIGURE 5. Input data of response variables

3. Generate experimental design

After the data for variables and response had been filled, Design Expert was used to generate the design layout which lists the experimental settings to be used for each experiment runs. The order for the experiment runs was randomized and it was followed to carry out the experiments. FIGURE 6 shows the order of experiment runs generated by Design Expert that were conducted in order to get the result for the responses. There are total 19 experimental runs generated by Design Expert.

After the experiments have been carried out, the results for percentage of nitrate removal were inserted to the response variable column.



Select	Std	Run	Factor 1 A:Initial Nitrat... mM	Factor 2 B:Weight of ... g	Factor 3 C:Contact Ti... h	Response 1 Percentage ... %
	14	1	0.15	0.275	24.00	
	16	2	0.15	0.275	12.50	
	11	3	0.15	0.050	12.50	
	9	4	0.05	0.275	12.50	
	3	5	0.05	0.500	1.00	
	5	6	0.05	0.050	24.00	
	6	7	0.25	0.050	24.00	
	8	8	0.25	0.500	24.00	
	2	9	0.25	0.050	1.00	
	4	10	0.25	0.500	1.00	
	12	11	0.15	0.500	12.50	
	15	12	0.15	0.275	12.50	
	1	13	0.05	0.050	1.00	
	17	14	0.15	0.275	12.50	
	13	15	0.15	0.275	1.00	
	19	16	0.15	0.275	12.50	
	7	17	0.05	0.500	24.00	
	18	18	0.15	0.275	12.50	
	10	19	0.25	0.275	12.50	

FIGURE 6. Experiment runs generated by Design Expert Software

Evaluating the design

The design model was then analysed using the evaluating tools in Design Expert such as analysis of variance (ANOVA) and Design-Expert plot. Both tools were used to estimate the error in the design but for the Design-Expert plot, the error was represented by graphical form. Therefore, by using these evaluating tools, the accuracy of the model design was then determined.

Generally, the response variable could be described by two types of models, either based on linear function or quadratic function. It was necessary to see whether the responses are well fitted to the linear or quadratic function. The linear equation was shown as follows [16]:

$$y = \beta_o \sum_{i=1}^{k} \beta_i x_i + \varepsilon \quad (1)$$

Where y = measured response.

k = number of variables

$\boldsymbol{\beta}_o$ = constant term

$\boldsymbol{\beta}_i$ = coefficients of linear parameters

x_i = variables

$\boldsymbol{\varepsilon}$ = residual error

Meanwhile, the quadratic model was represented by the following equation:

$$y = \beta_o \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} B_{ii} x_i^2 + \sum_{1 \le i \le j}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

Where $\boldsymbol{\beta}_{ii}$ = coefficients of the quadratic parameter

$\boldsymbol{\beta}_{ij}$= coefficients of the interaction parameters

Besides, Design Expert also suggested the type of model for the response based on ANOVA results as well as the variance of the predicted value and actual value.

Optimization

After the accuracy and validity of the model had been verified, optimization of the variables was then proceeded. The optimization could be carried out by several methods such as numerical, graphical or point prediction. In this study, numerical optimization was used due to its simplicity. The optimization was done just by setting a set of goals for each variables and responses in the software, Design Expert. Based on the goals, the software generated a list of possible solutions with optimum condition for the nitrate removal process using the synthesized adsorbents.

3.3 Synthesis of 20% loaded AEPTMS-MCM 41 adsorbent

The experimental procedures for the synthesis of MCM-41 loaded with 20% AEPTMS were as follows [57]:

1. The reaction mixtures was prepared based on the molar ratio of CTAB:TEOS:AEPTMS:NaOH:H_2O (1:7.37:1.84:2.55:4857). The amount of reactants required was simplified in TABLE 3.
2. First, the mixture of CTAB, NaOH and H_2O was prepared according to the ratio and heated at 80 ℃ for 30 minutes. Then, TEOS and AEPTMS were added sequentially and rapidly.
3. The temperature of reaction mixture was maintained at 80 ℃ for 2 hours.
4. After 2 hours, the reaction mixture was centrifuged, washed with plenty amount of water, and then dried in oven.
5. An acid extraction was performed in a methanol (100 mL) mixture of concentrated hydrochloric acid (1 mL) and the product materials (1 g) at 60 ℃ for 6 hours.
6. Finally, the resulting surfactant-removed solid products was centrifuged again and washed with water and methanol, and then dried in the oven.

TABLE 3. Amount of reactants required for the synthesis of 20% loaded AEPTMS MCM-41

Reactants	**Required Amount**
Cetryltrimethylammonium bromide (CTAB)	2 g (5.49 mmol)
Tetraethoxysilane (TEOS)	8.452 g (40.44 mmol)
3-[2-(2-aminoethylamino)ethylamino] propyltrimethoxysilane (AEPTMS)	2.683 g (10.11 mmol)
Sodium Hydroxide (NaOH)	7 mL (2 M, 14 mmol)
De-ionized water (H_2O)	480 g (26.67 mol)

3.4 Characterization

3.4.1 Fourier Transform Infrared Spectroscopy (FTIR) *[Model: Shimadzu 8400s]*

Fourier Transform Infrared Spectroscopy **(**FTIR) is a widely used method to identify the functional groups in a certain sample. First, it will obtain infrared spectra by collecting an interferogram of a sample signal using interferometer. Then, the interferogram collected will be sent to FTIR spectrometer to be digitized. Fourier Transform (FT) is performed to obtain the spectrum by using wavelength of 400 to 4000 cm^{-1}. The spectrum produced by the FTIR represents the molecular absorption and transmission, creating a molecular fingerprint of the sample.

3.4.2 Scanning Electron Microscope (SEM) *[Model: Hitachi TM 3030]*

Scanning Electron Microscope (SEM) is a type of instrument used for analysis of microstructural characteristics of solid samples. It can provide three-dimensional image of the specimen appearance in high resolution [58]. In this work, SEM will be used to analyse the morphology and surface structure of 20% loaded AEPTMS MCM-41.

3.4.3 UV-Vis Spectroscopy *[Model: Cary 60]*

UV-Vis Spectroscopy is commonly used to identify functional groups and measure concentration of solutions. It will generate a graph representing transmittance as a function of wavelength. In this study, UV-Vis Spectroscopy was used to determine the final nitrate concentration.

3.5 Nitrate Removal Test

3.5.1 Adsorption Study

The experiments were carried out according to the order suggested by DoE software as shown in FIGURE 6, where initial nitrate concentration, weight of adsorbents and contact time of adsorbent is represented by A, B and C respectively. The uptake of nitrate using the adsorbents synthesized in the present work was carried out as follows [25]:

1. 25 mL of A mM sodium nitrate ($NaNO_3$) solution was added to B g of adsorbent in conical flask to carry out a batch equilibration study.
2. The mixture was shaken by hand for one or two minutes before thoroughly mixed using stirrer for C hours.
3. After C hours of equilibration, the solid and solution phases were separated by using glass syringe through a 5 μm nylon filter.
4. 15 mL of each solution was collected in clean vial for nitrate analysis.
5. The percentage removal of nitrate at equilibrium was calculated using equation (3) as follows [37]:

$$R\ (\%) = \frac{(C_i - C_e)}{C_i}\ x\ 100\% \tag{3}$$

Where R = percentage of nitrate removal (%)

C_i = initial concentration of nitrate in solution (mM)

C_e = final (equilibrium) concentration of nitrate in solution (mM)

6. The nitrate adsorption capacity of the adsorbents at equilibrium was calculated using equation (4) as follows [25]:

$$q_e = (C_i - C_e)\ x\ \frac{V}{m} \tag{4}$$

Where q_e = adsorption capacity (mg NO^{-3}/g adsorbent)

V= Volume of solution (L)

m = mass of adsorbent (g)

7. Step 1 to Step 6 was repeated using other experimental conditions suggested by DoE software.

3.5.2 Isotherms Study

Adsorption isotherm study was carried out to study the distribution of nitrate between solution and adsorbent at the equilibrium state of the adsorption process. In this work, two models were used to study the adsorption behaviour of nitrate, namely Langmuir isotherm and Freundlich isotherm. The model generated by DoE software was used to determine the necessary parameters for adsorption isotherms study. Then, the data was tested if they fit for Langmuir isotherm or Freundlich isotherm.

Equation 7 describes Langmuir isotherm [59]:

$$\frac{1}{q_e} = \frac{1}{q_m K_L}\frac{1}{C_e} + \frac{1}{q_m} \tag{5}$$

Where q_e = amount of nitrate adsorbed per mass unit of adsorbent at equilibrium (mg/g)

C_e = equilibrium concentration of the remaining solution (mg/l)

K_L = Langmuir constant (l/mg)

q_m = amount of nitrate adsorbed per mass unit of adsorbent at complete monolayer coverage (mg/g)

By plotting the graph of $1/q_e$ versus $1/C_e$, the maximum adsorption capacity (q_m) and Langmuir constant (K_L) can then be determined.

Freundlich isotherm model is described by the following equations [25]:

$$q_e = K_F C_e^{1/n} \tag{6}$$

$$log\ q_e = logK_F + \frac{1}{n} logC_e \tag{7}$$

Where K_F and n are Freundlich adsorption isotherm constants which can be determined from slope and intercept of the graph respectively.

3.6 Equipment and Chemicals Used

3.6.1 Equipment and Apparatus

1. Hot Plate Stirrer
2. Oven
3. Centrifuge
4. Glass syringe with filter
5. FTIR Spectrometer
6. SEM

3.6.2 Chemicals

1. 3-[2-(2-aminoethylamino)ethylamino]proplytrimethoxysilane (AEPTMS)
2. Cetryltrimethylammonium bromide (CTAB)
3. Tetraethoxysilane (TEOS)
4. Sodium Hydroxide (NaOH)
5. Methanol (CH_3OH)
6. Hydrochloric acid (HCl)
7. De-ionized water (H_2O)
8. Sodium Nitrate ($NaNO_3$)

3.6.3 Software

1. Design Expert version 6.0.6

3.7 Milestones

TABLE 4 shows the key milestones of FYP I:

TABLE 4. FYP I and II Key Milestones

Semester	Tasks	Completion
May 2015	Research for literature reviews	Week 6
	Submission of extended proposal	Week 7
	Proposal defense	Week 9
	Familiarization of DoE software	Week 10
	Submission of interim draft report	Week 12
	Submission of interim final report	Week 13
	Synthesis of functionalized MCM-41	Week 14
September 2015	Characterization of functionalized MCM-41	Week 2
	Nitrate removal test	Week 5
	Optimization study using DoE software	Week 7
	Submission of progress Report	Week 8
	Data analysis	Week 10
	Pre-Sedex	Week 11
	Submission of draft report	Week 11
	Submission of dissertation (soft bound)	Week 12
	Submission of technical paper	Week 12
	Viva Oral Presentation	Week 13
	Submission of Project Dissertation (Hard Bound)	Week 14

3.8 Activities Gantt Chart

TABLE 5 shows the activities Gantt Chart of FYP I:

TABLE 5. FYP I Gantt Chart

No	Activities / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.	Topic Selection														
2.	Preliminary Research Work														
3.	Submission of Extended Proposal														
4.	Proposal Defence														
5.	Familizarization of DoE software														
6.	Synthesis of functionalized MCM-41														
7.	Submission of Interim Draft Report														
8.	Submission of Interim Final Report														

TABLE 6 shows the activities Gantt Chart of FYP II:

TABLE 6. FYP II Gantt Chart

No	**Activities** / **Week**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
1.	Characterization of functionalized MCM-41														
2.	Nitrate removal test														
3.	Optimization study using DoE software														
4.	Data analysis														
5.	Submission of progress Report														
6.	Pre-Sedex														
7.	Submission of draft report														
8.	Submission of dissertation (soft bound)														
9.	Submission of technical paper														
10.	Viva Oral Presentation														
11.	Submission of Project Dissertation (Hard Bound)														

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Characterization

4.1.1 Fourier Transform Infrared Spectroscopy (FTIR)

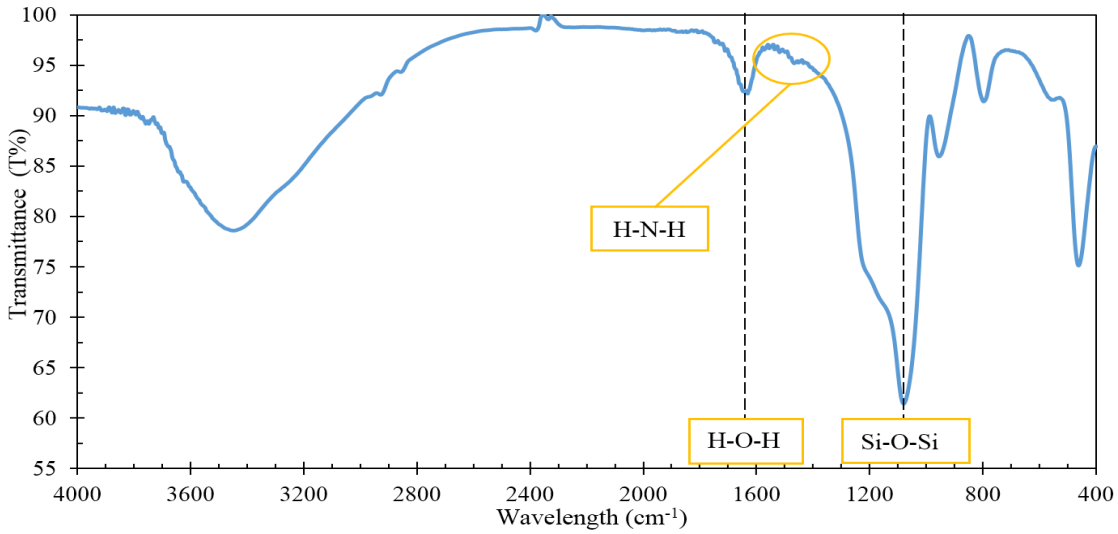


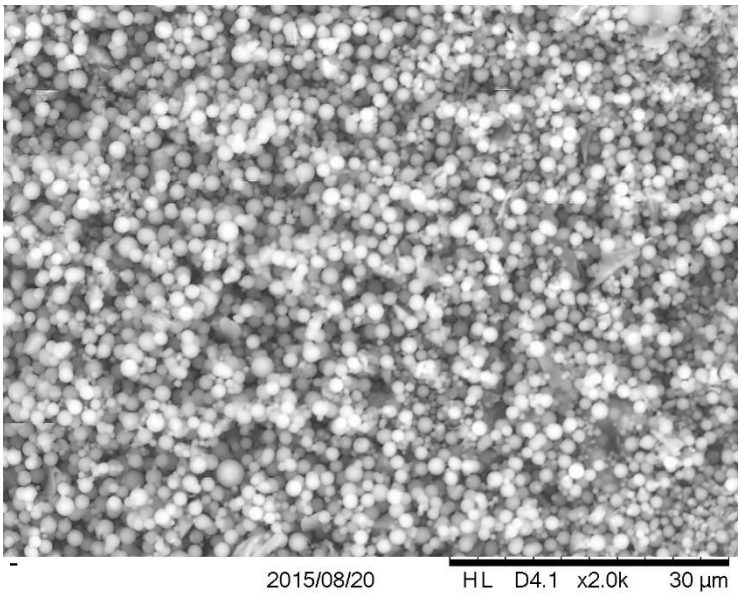
FIGURE 7. FTIR Spectra for 20% AEPTMS amine-functionalized MCM-41 adsorbent

FIGURE 7 shows the FTIR spectra of the synthesized adsorbent (20% AEPTMS amine-functionalized MCM-41). Strong absorption band is observed near 1050 cm^{-1} to 1100 cm^{-1} due to the Si-O stretching vibrations in Si-O-Si structure, which is the structural characteristic of silica [60, 61]. The absorption band from 1620 – 1650 cm^{-1} indicates H-O-H bending vibration of water molecules [60, 62], meanwhile, the broad band at 3100-3600 cm^{-1} is attributed to the adsorbed water molecules [60]. The presence of $–NH_2$ symmetric vibration at around 1500 cm^{-1} indicates the successful functionalization of amine onto the mesoporous silica MCM-41 surface [62]. Besides, the amine functionalized MCM-41 also shows the characteristic of asymmetric vibration of the CH_2 groups at 2900 cm^{-1} [61].

4.1.2 Scanning Electron Microscope (SEM)

The surface morphology of 20% AEPTMS amine-functionalized MCM-41 is studied using Scanning Electron Microscope (SEM). FIGURE 8 shows the morphology of the adsorbent with different magnifications. The particles are spherical in shape, well ordered and arranged. This is consistent with the SEM images reported in the literature [60]. The particles size obtained is around 1.50 to 2 μm.

(a)



(b)

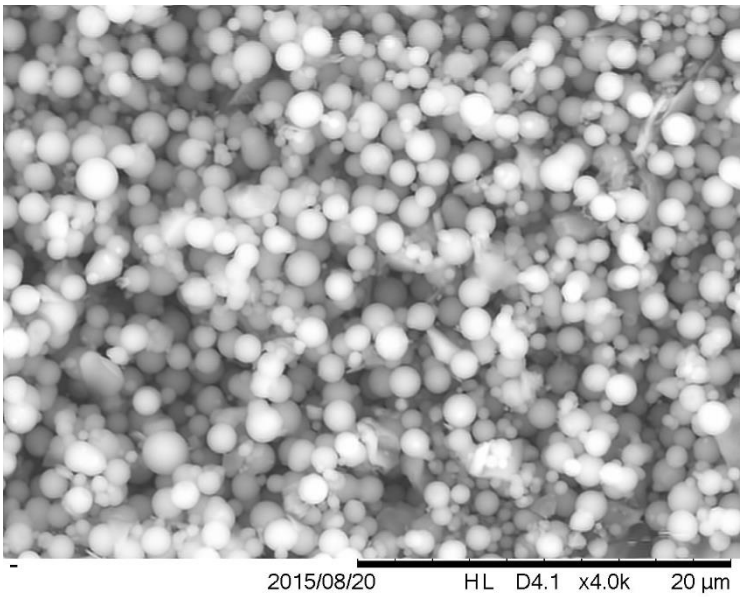


FIGURE 8. SEM images of 20% AEPTMS amine-functionalized MCM-41 a) Magnification: x2.0k and b) Magnification: x4.0k

4.2 Nitrate Removal Study

4.2.1 Statistical Model Analysis

Response Surface Methodology (RSM) was used to correlate the interactions between the independent variables (A, B, C) and response (Y) in the nitrate removal study using 20% AEPTMS amine-functionalized MCM-41. The final nitrate concentration was tested using UV-Vis spectrophotomer after the removal test. TABLE 7 tabulates the results of the response by each experimental run suggested by RSM. It is shown that the highest percentage of nitrate removal is around 70% obtained using initial nitrate concentration of 0.25 mM, adsorbent dosage of 0.50 g and contact time of 1 h. This proves that the adsorption capacity of 20% AEPTMS functionalized MCM-41 is much better than that of pure MCM-41, which could only achieve up to 20% of nitrate removal [25].

TABLE 7. Nitrate Removal Experiment Runs and Responses

Exp run	A: Initital Nitrate Concentration (mM)	B: Weight of Adsorbents (g)	C: Contact Time (h)	Y: Nitrate Removal (%)
1	0.15	0.275	24.00	46.86
2	0.15	0.275	12.50	47.00
3	0.15	0.050	12.50	26.25
4	0.05	0.275	12.50	9.40
5	0.05	0.500	1.00	19.52
6	0.05	0.050	24.00	20.73
7	0.25	0.050	24.00	43.98
8	0.25	0.500	24.00	69.29
9	0.25	0.050	1.00	45.07
10	0.25	0.500	1.00	70.26
11	0.15	0.500	12.50	47.41
12	0.15	0.275	12.50	46.86
13	0.05	0.050	1.00	4.16
14	0.15	0.275	12.50	42.67
15	0.15	0.275	1.00	46.51
16	0.15	0.275	12.50	43.05
17	0.05	0.500	24.00	20.53
18	0.15	0.275	12.50	47.80
19	0.25	0.275	12.50	65.69

TABLE 8. ANOVA results for the models evaluation

Model terms	Sum of Squares	Mean Square	F Value	Prob > F
Model	6330.78	486.98	58.99	0.0001
A	1584.28	1584.28	191.91	< 0.0001
B	223.87	223.87	27.12	0.0034
C	0.061	0.061	7.419E-003	0.9347
AB	156.11	156.11	18.91	0.0074
AC	48.22	48.22	5.84	0.0604
BC	29.80	29.80	3.61	0.1159
A^2	82.27	82.27	9.97	0.0252
B^2	105.11	105.11	12.73	0.0161
C^2	36.46	36.46	4.42	0.0896
ABC	30.73	30.73	3.72	0.1116
A^2B	9.01	9.01	1.09	0.3441
A^2C	4.98	4.98	0.60	0.4723
AB^2	94.56	94.56	11.45	0.0196
Lack of Fit	17.88	17.88	3.06	0.1553

TABLE 8 shows the ANOVA results used to test the accuracy of the fitted models. The model was selected based on the highest order polynomial where the additional terms are significant and the model is not aliased. In this study, a quadratic model was suggested by the DoE software with F-value of 58.99 and "Prob > F" of 0.0001. This implies that the model is significant at 95% confidence level as the calculated probability is lower than 0.05.

Besides, for the model term to be significant, the calculated probability should be lower than 0.05 ("Prob > F" less than 0.0500). In this case, A, B, AB, A^2, B^2, AB^2 are all significant model terms for percentage of nitrate removal while C, AC, BC, C^2, ABC, A^2B, A^2C are insignificant to percentage of nitrate removal. This indicates that initial nitrate concentration (A) and weight of adsorbent (B) have significant influence on the nitrate removal process while the contact time of adsorbent has little or no effect to the percentage of nitrate removal.

On the other hand, The "Lack of Fit F-value" of 3.06 indicates the lack of fit is insignificant. This implies that the model fits the experiment data and it is adequate to make precise prediction on the data behaviour in the present study.

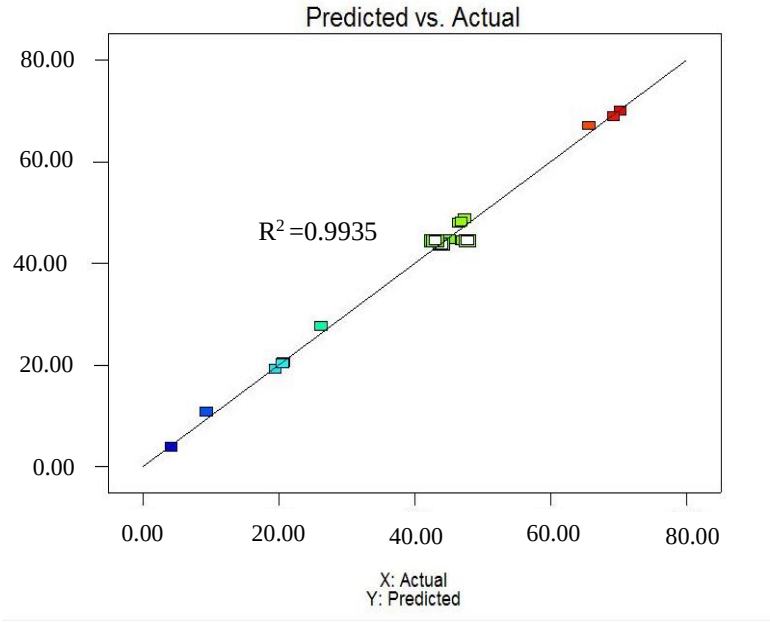


FIGURE 9. Predicted versus Actual Design Expert Plot

FIGURE 9 shows Design Expert plot on the predicted versus actual values of nitrate removal percentage. The straight line indicates the predicted values while the small boxes represent the actual experimental values. The straight line is located very close to the actual values and has a correlation coefficient, R^2 of 0.9935, confirming the accuracy of the model.

The quadratic model used for percentage of nitrate removal (Y) are described in Equation 8 and Equation 9 in terms of coded factors and actual factors, respectively:

Percentage of nitrate removal (%), Y (coded factors) =
+44.39+28.15 * A
+10.58 * B
+0.18 * C
+4.42 * A * B
-2.45 * A * C
-1.93 * B * C
-5.49 * A^2
-6.20 * B^2
+3.65 * C^2
+1.96 * A * B * C
-2.37 * A^2 * B
+1.76 * A^2 * C
-7.69 * A * B^2 (8)

Percentage of nitrate removal (%), Y (actual factors)

$$
\begin{aligned}
&-11.18507 \\
&+300.52452 * A \\
&-40.52132 * B \\
&+0.50785 * C \\
&+1253.16586 * A * B \\
&-8.82222 * A * C \\
&-1.88213 * B * C \\
&-450.60241 * A^2 \\
&+105.26384 * B^2 \\
&+0.027620 * C^2 \\
&+7.57488 * A * B * C \\
&-1054.44444 * A^2 * B \\
&+15.34783 * A^2 * C \\
&-1518.51852 * A * B^2
\end{aligned} \tag{9}
$$

Where equation 11 is subjected to $0.05\ \text{mM} \leq A \leq 0.25\ \text{mM}$, $0.05\ \text{g} \leq B \leq 0.50\ \text{g}$ and $1\ \text{h} \leq C \leq 24\ \text{h}$

The percentage of nitrate removal plots for the three variables have been predicted based on the model. Figures 10-12 show three-dimensional plots for the interaction between percentage of nitrate removal and the variables. The interaction between the initial nitrate concentration and weight of adsorbent at fixed contact time of 12.50 hours can be seen from FIGURE 10.

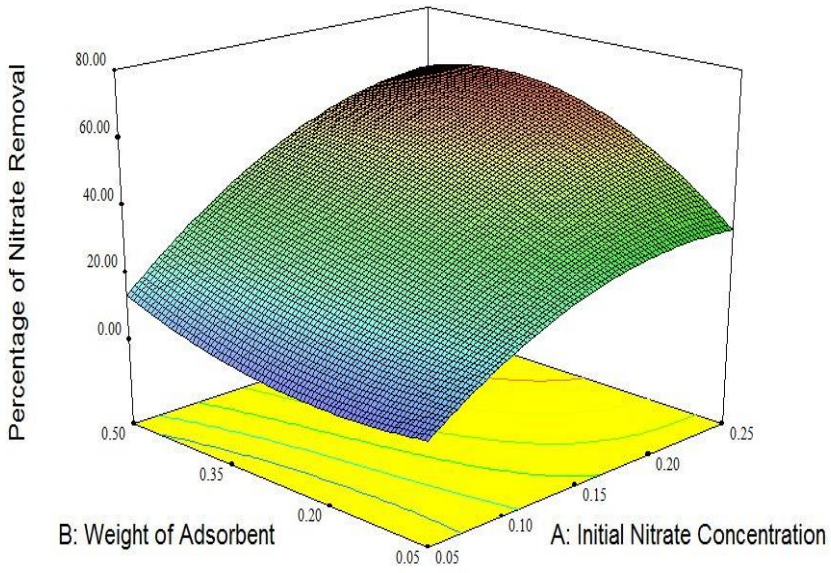


FIGURE 10. Percentage of Nitrate Removal against Weight of Adsorbent and Initial Nitrate Concentration at Contact time of 12.5 h

From FIGURE 10, it can be seen that both of the parameters exhibit great effect on the nitrate removal process. As the initial nitrate concentration increases, the percentage of nitrate removal increases proportionally. This can be explained by the gradient of nitrate adsorbed concentration, where the concentration gradient increases as the initial nitrate concentration increases. The higher concentration gradient acts as a driving force to overcome the mass transfer resistance between bulk solution and adsorbent surface [63]. This in turn leads to higher nitrate adsorption efficiency.

On the other hand, the weight of adsorbent seems to have little or no effect on nitrate removal test at very low initial nitrate concentration. However, as the initial nitrate concentration increases, the percentage of nitrate removal increases with increase in weight of adsorbent. This proves that weight of adsorbent also has a significant effect in the nitrate removal process when the initial nitrate concentration increases. The increase in percentage of nitrate removal is mainly due to the increase in the total available adsorbent surface area and adsorption sites with increasing adsorbent weight [38].

Besides, at the highest concentration of 0.25 mM and highest adsorbent weight of 0.50 g, the highest percentage of nitrate removal is attained. In summary, it is concluded that the percentage of nitrate removal is increased by increasing both the initial nitrate concentration and weight of adsorbent.

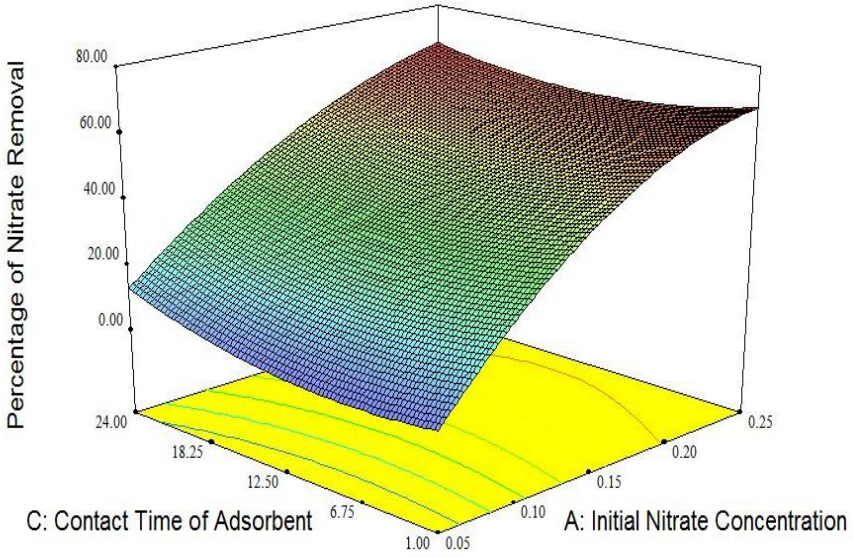


FIGURE 11. Percentage of Nitrate Removal against Contact Time of Adsorbent and Initial Nitrate Concentration at Weight of Adsorbent of 0.275 g

FIGURE 11 shows the effect of contact time of adsorbent and initial nitrate concentration on the nitrate removal test at a constant adsorbent weight of 0.275 g. It can be seen that the percentage of nitrate removal is significantly affected by initial nitrate concentration at any contact time. This is in agreement with the result from FIGURE 10, whereby the steeper the gradient of nitrate adsorbed concentration, the higher the percentage of nitrate removal [63].

However, the percentage of nitrate removal does not increase with increasing contact time of adsorbent at any initial nitrate concentration. It can be inferred that the adsorbent has reached the maximum adsorption capacity within one hour. In other words, the surface coverage of the adsorbent is already saturated in less than one hour. Therefore,

it can be concluded that the percentage of nitrate removal is independent on the contact time of adsorbent between 1 h to 24 h in the present study.

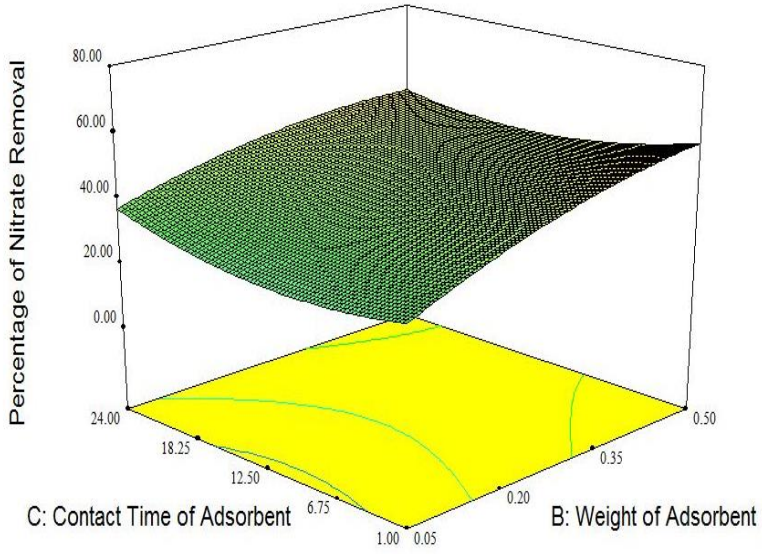


FIGURE 12. Percentage of Nitrate Removal against Contact Time of Adsorbent and Weight of Adsorbent at Initial Nitrate Concentration of 0.15 mM

FIGURE 12 shows the effect of contact time of adsorbent and weight of adsorbent on the percentage of nitrate removal at constant initial nitrate concentration of 0.15 mM. It is observed from the figure that the percentage of nitrate removal does not increase by increasing the contact time of adsorbent. For example, as seen from FIGURE 12, the percentage of nitrate removal is almost the same for contact time of 1.00 h, 12.50 h and 24.00 h at 0.05 g of adsorbent. Hence, it could be mainly due to saturation of the adsorption capacity of the adsorbent after 1 h of contact time.

On the other hand, it can be seen that the percentage of nitrate removal increases with increasing weight of adsorbent at any contact time between 1-24 h. This is due to the larger total available adsorbent surface area and increased amount of adsorption sites as explained in FIGURE 10 earlier [38]. From here, it can be concluded that the percentage of nitrate removal is highly dependent on the weight of adsorbent but independent on contact time of adsorbent between 1-24h.

4.2.2 Optimization

In the present study, numerical optimization in the DoE software was chosen to optimize the experimental conditions in nitrate removal process. Goal was set for each criteria including the three variables and one response. TABLE 9 shows the pre-set values for each criteria.

TABLE 9. Optimization goal for different criteria in nitrate removal study

Criteria	Goal	Lower Limit	Upper Limit
Initial Nitrate Concentration, mM	In the range	0.05	0.25
Weight of Adsorbent, g	Minimize	0.05	0.50
Contact time of Adsorbent, h	Minimize	1.00	24.00
Percentage of Nitrate Removal, %	Maximize	4.16	70.26

For initial nitrate concentration, the goal was set in the range. The weight of adsorbent was set to be minimized for the purpose of cost saving, while the contact time was set to be minimized in order to make sure the removal process is efficient in term of time. The percentage of nitrate removal was set as maximum in order to achieve the maximum nitrate adsorption capability.

From the goal set, there were a list of optimization solutions generated by Design Expert software. TABLE 10 shows 18 optimum conditions found by the software. The optimum condition with the highest desirability of 0.871 and highest percentage of nitrate removal is selected for the optimization studies. The optimum condition shows 0.25 mM of initial nitrate concentration, 0.124 g of adsorbent, and 1.00 hour of contact time. Total of 4 experiments were conducted at the optimum condition to verify the accuracy of the prediction. TABLE 11 shows the results of the 4 repeated experiments. The experimental results are close to the predicted values with average percentage error of 6.27%.

TABLE 10. Optimum conditions generated by DoE for nitrate removal process using 20% AEPTMS amine-functionalized MCM-41.

Solution	A: Initial Nitrate Concentration, mM	B: Weight of Adsorbent, g	C: Contact Time, h	Y: Percentage of Nitrate Removal, %	Desirability
1	0.25	0.124	1.00	56.4671	0.871
2	0.25	0.120	1.00	55.9974	0.871
3	0.25	0.128	1.00	57.1020	0.871
4	0.25	0.122	1.00	56.2073	0.871
5	0.25	0.126	1.01	56.8181	0.871
6	0.25	0.146	1.00	59.4289	0.870
7	0.25	0.154	1.00	60.4541	0.868
8	0.25	0.110	1.28	54.3179	0.866
9	0.25	0.142	1.27	58.7577	0.866
10	0.25	0.085	1.00	50.5950	0.866
11	0.25	0.169	1.00	62.2338	0.864
12	0.25	0.140	1.47	58.2969	0.863
13	0.25	0.102	1.48	53.0589	0.862
14	0.25	0.179	1.00	63.3198	0.861
15	0.25	0.065	1.00	47.3359	0.858
16	0.25	0.102	1.00	50.8932	0.855
17	0.25	0.227	1.73	67.9304	0.826
18	0.25	0.159	1.00	51.5343	0.816

TABLE 11. Experiment verification for optimum conditions in nitrate removal process

Run	Y: Percentage of Nitrate Removal, %	Error, %
1	61.62	9.12
2	59.57	5.49
3	57.88	2.51
4	60.96	7.96
Average	**60.01**	**6.27**

4.2.3 Adsorption Isotherms Study

In this study, Langmuir and Freundlich models were used to study the adsorption behaviour of nitrate as these two are the most commonly used models. The mutual correlation of adsorption capacity and equilibrium concentration was studied by fitting the experimental data using Langmuir and Freundlich isotherm models respectively. Based on the equation model developed in the section earlier, the isotherms study is carried out at different initial nitrate concentration of 0.05 mM, 0.10 mM, 0.15 mM, 0.20 mM and 0.25 mM at fixed contact time of 1 h. These studies were performed at different adsorbent dosage of 0.05 g, 0.275 g and 0.50 g.

FIGURE 13 shows the Langmuir isotherms plots with different adsorbent dosages. Based on these plots, it can be seen that the isotherm data of 20% AEPTMS amine-functionalized MCM-41 with dosage of 0.05 g, 0.275 g and 0.50 g fits the Langmuir equation with correlation coefficients of 0.9324, 0.9816 and 0.9974 respectively. It is also observed that as the adsorbent dosage increases, the isotherms data fits better and the linearity increases. TABLE 12 shows the Langmuir parameters for different dosage of the adsorbent at fixed contact time of 1 h.

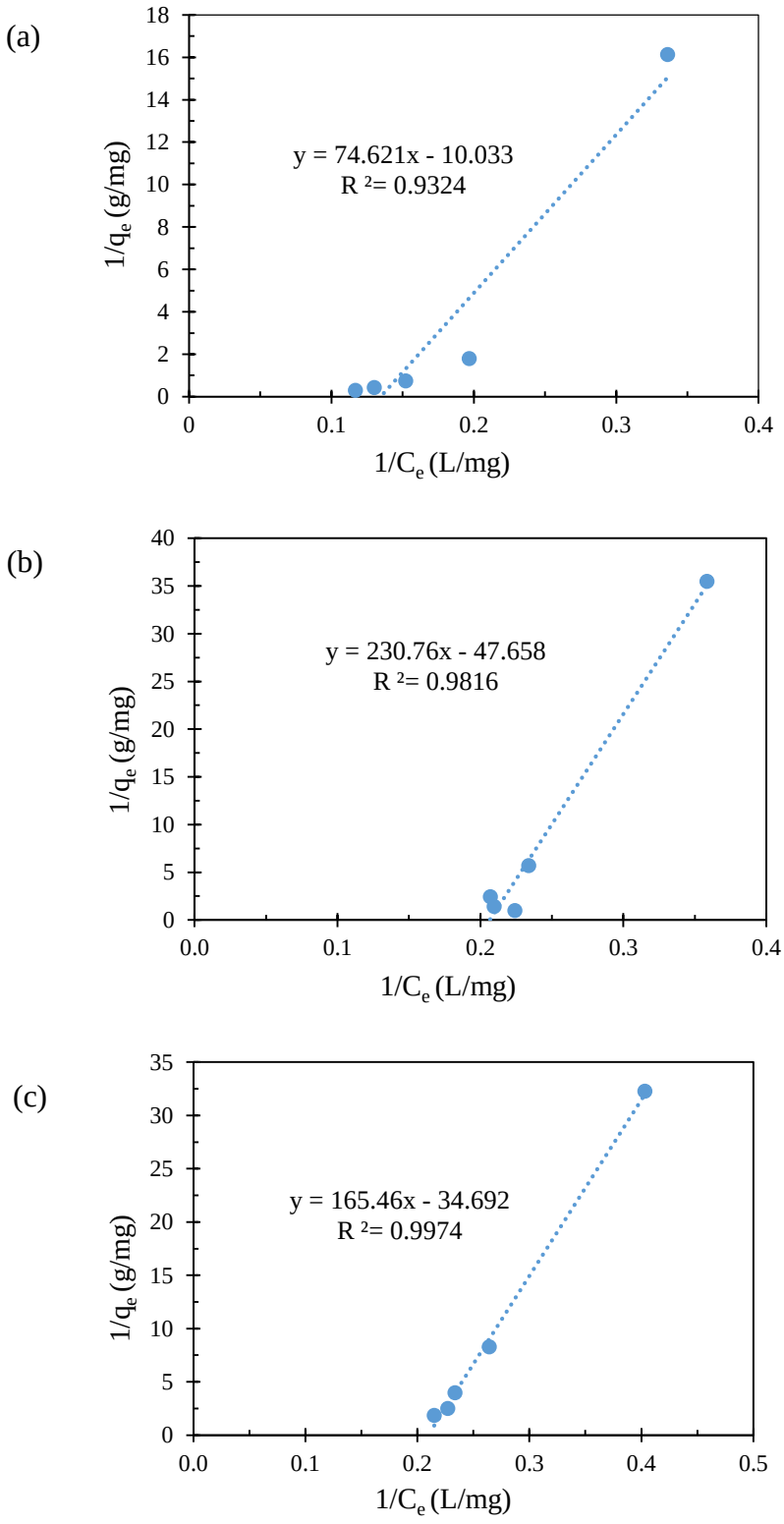


FIGURE 13. Langmuir isotherm plots for nitrate adsorption by 20% AEPTMS amine-functionalized MCM-41with different adsorbent dosage: (a) 0.050 g (b) 0.275 g (c) 0.500 g

TABLE 12. Langmuir parameters of studied samples

Adsorbent dosage (g)	**q_m (mg/g)**	**K_L**	**R^2**
0.050	-0.09967	-0.13345	0.9324
0.275	-0.02098	-0.20655	0.9816
0.500	-0.02883	-0.20963	0.9974

From TABLE 12 and FIGURE 13, it can be observed that at all adsorbent dosages, the Langmuir parameters have negative values even though the correlation coefficient, R^2 obtained is sufficiently high. It is evident that Langmuir isotherms failed to explain the adsorption behaviour of nitrate using 20% AEPTMS amine-functionalized MCM-41. Langmuir isotherms assumes the adsorbent surface is homogeneous and there are no interactions between adsorbate molecules on adjacent sites [25]. Therefore, it is believed that the surface of 20% AEPTMS amine-functionalized MCM-41 synthesized in the present work is non-homogeneous.

On the other hand, the experimental data predicted from the model also used to fit Freundlich isotherm. FIGURE 14 shows Freundlich isotherm plots at different adsorbent dosages.

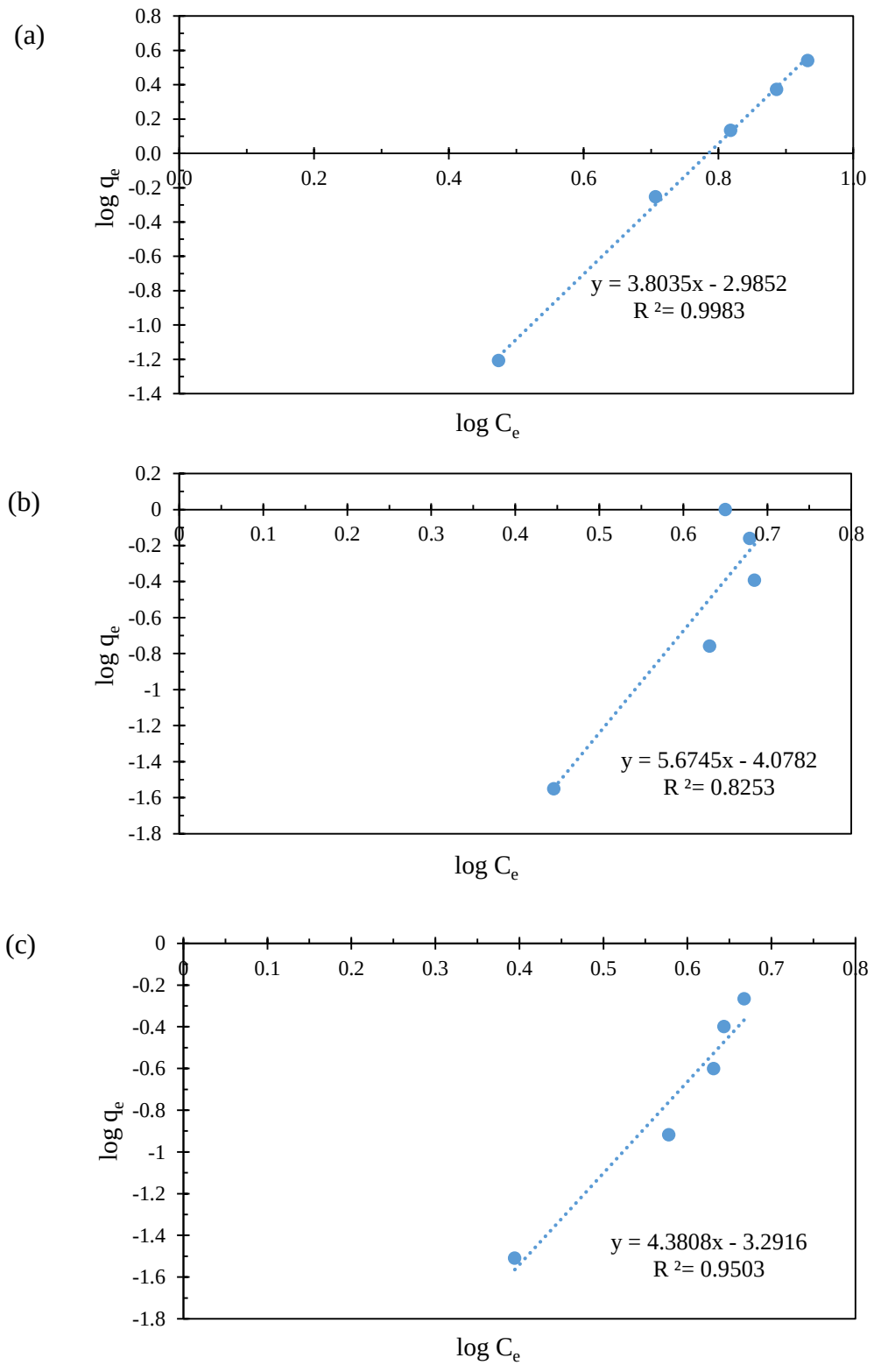


FIGURE 14. Freundlich isotherm plots for nitrate adsorption by 20% AEPTMS amine-functionalized MCM-41with different adsorbent dosage: (a) 0.050 g (b) 0.275 g and (c) 0.500 g

The Freundlich isotherm constants K_F and *n* were calculated based on the graphs and shown in TABLE 13.

TABLE 13. Freundlich parameters of the studied sample at different adsorbent dosage

Adsorbent dosage (g)	**K_F**	***n***	**R^2**
0.050	0.00103	0.2629	0.9983
0.275	0.00008	0.1762	0.8253
0.500	0.00051	0.2283	0.9503

Based on TABLE 13, it can be seen that Freundlich isotherm fits the isotherm data of 20% AEPTMS amine-functionalized MCM-41 with high correlation coefficient, R^2. It is also observed that the correlation coefficient, R^2 is the highest at the lowest adsorbent dosage (R^2 = 0.9983). This implies that Freundlich isotherm best describes the adsorption behaviour of nitrate at low adsorbent dosage. With the acceptable range of correlation coefficient, R^2 for Freundlich isotherms and negative constants obtained from Langmuir isotherms, it can be deduced that the isotherm data of 20% AEPTMS amine-functionalized MCM-41 fits Freundlich isotherm better than Langmuir isotherm.

The main reason could be mainly due the heterogeneous surface of the adsorbent as described by Freundlich isotherm. Freundlich isotherm assumes non-ideal adsorption of heterogeneous system and reversible adsorption. A value of *n* above 1 indicates normal Freundlich isotherms while *n* below 1 indicates cooperative adsorption [25]. In the present study, the n values obtained from Freundlich isotherms for all the adsorbent dosages are ranged from 0.1762 to 0.2629, indicating cooperative adsorption occurred in the nitrate removal process. On the other hand, the smaller values of *n* obtained also indicates a stronger bond exists between adsorbate and adsorbent [59].

CHAPTER 5
CONCLUSION & RECOMMENDATIONS

5.1 Conclusion

Increasing nitrate concentration in ground water has been a very serious issues since the last few decades. It poses a serious threat to both human health and environment. High concentration of nitrate in ground water can cause eutrophication and subsequently cause the death of aquatic animals [26]. On the other hand, drinking water contaminated by nitrate may cause hair loss, skin rashes, birth defect and also "blue baby syndrome" [22, 28]. Up to today, various methods have been developed to remove nitrate from aqueous solution. The recent study has found that 20% AEPTMS amine-functionalized MCM-41 has high capability to remove nitrate from aqueous solution [13]. However, the experimental conditions in the nitrate adsorption process are yet to be optimized. Hence, the present work aims to optimize the experimental conditions including, initial nitrate concentration, weight of adsorbent, contact time of adsorbent by using Response Surface Methodology (RSM).

Based on the result from the present study, it is shown that 20% AEPTMS amine-functionalized MCM-41 has been successfully synthesized through co-condensation method. The surface morphology of the adsorbent has been verified with Scanning Electron Microscope and it is consistent with the SEM images reported from the literature [60]. Besides, FTIR spectra also showed that the functionalization of amine onto the mesoporous silica MCM-41 surface is successful [61, 62].

The nitrate removal study has been carried out according to the experimental conditions suggested by DoE software. There were total of 19 experiments subjected to

the experimental conditions of 0.05 mM ≤ initial nitrate concentration ≤ 0.25 mM, 0.05 g ≤ weight of adsorbent ≤ 0.50 g, 1 h ≤ contact time of adsorbent ≤ 24 h. From the result, 20% AEPTMS MCM-41 could achieve up to 70% of nitrate removal, which is much higher than the pure MCM-41 reported from the literature [25].

Besides, the optimization study on the nitrate removal process also has been successfully conducted by using Response Surface Methodology (RSM). Based on the experimental result, the DoE software has developed a model to represent the experimental data. The model is analyzed to be significant with F-value of 0.0001 and correlation coefficient, R^2 of 0.9935. The interaction between the three variables, initial nitrate concentration, weight of adsorbent, contact time of adsorbent and the response, percentage of nitrate removal has been demonstrated in 3D surface plot through prediction from the model. Percentage of nitrate removal of 56% was obtained at the optimum conditions with initial nitrate concentration of 0.25 mM, weight of adsorbent of 0.124 g and contact time of 1 h. The optimum condition was repeated with experiments and the results were in good agreement with the predicted data, showing accuracy of the model.

Lastly, adsorption isotherms study also has been conducted to study the nitrate adsorption behavior. Freundlich isotherms explained the adsorption process better than Langmuir isotherm. Therefore, it is believed that the surface of 20% AEPTMS amine-functionalized MCM-41 is non-homogeneous and there are interactions between adsorbate molecules on the adjacent sites.

5.2 Recommendations

For future recommendation, a study can be performed to determine the optimum temperature and pH in nitrate removal process using 20% AEPTMS amine-functionalized MCM-41 by Response Surface Methodology. Besides, it is also suggested that the nitrate adsorption study should be carried out within the range of 1 hour as 20% AEPTMS amine-functionalized MCM-41 is found to be saturated after contact time of 1 hour in the present study. It is expected that with the improvements done, the nitrate adsorption efficiency can be further maximized. Subsequently, the removal of nitrate by using 20% AEPTMS loaded MCM-41 with optimum experimental conditions would be a new, feasible, cost-effective and environmental friendly approach.

REFERENCES

[1] N. N. Rabalais, R. E. Turner, and D. Scavia, "Beyond Science into Policy: Gulf of Mexico Hypoxia and the Mississippi River," *BioScience,* vol. 52, pp. 129-142, 2002.

[2] D. Scavia and K. A. Donnelly, "Reassessing hypoxia forecasts for the Gulf of Mexico," *Environmental science & technology,* vol. 41, pp. 8111-8117, 2007.

[3] S. Mousavi, S. Ibrahim, M. K. Aroua, and S. Ghafari, "Development of nitrate elimination by autohydrogenotrophic bacteria in bio-electrochemical reactors–A review," *Biochemical Engineering Journal,* vol. 67, pp. 251-264, 2012.

[4] S. Ghafari, M. Hasan, and M. K. Aroua, "Bio-electrochemical removal of nitrate from water and wastewater—a review," *Bioresource Technology,* vol. 99, pp. 3965-3974, 2008.

[5] N. Öztürk and T. E. l. Bektaş, "Nitrate removal from aqueous solution by adsorption onto various materials," *Journal of hazardous materials,* vol. 112, pp. 155-162, 2004.

[6] "Washington State Department of Health. Guidance Document: Nitrate Treatment Alternatives for Small Water Systems," D. PUB, Ed., ed, 2005, pp. 331-309.

[7] A. Bhatnagar and M. Sillanpää, "A review of emerging adsorbents for nitrate removal from water," *Chemical Engineering Journal,* vol. 168, pp. 493-504, 2011.

[8] P. Westerhoff and K. Doudrick, "Treatment Technologies for Today and Tomorrow," *Nitrates in Ground Water,* vol. 8, 2009.

[9] S. Hamoudi and K. Belkacemi, "Adsorption of nitrate and phosphate ions from aqueous solutions using organically-functionalized silica materials: Kinetic modeling," *Fuel,* vol. 110, pp. 107-113, 2013.

[10] G. Castruita-de León, Y. A. Perera-Mercado, L. A. García-Cerda, J. A. Mercado-Silva, H. I. Meléndez-Ortiz, Y. Olivares-Maldonado, *et al.*, "Synthesis of amino-functionalized MCM-48 silica via direct co-condensation at room temperature," *Microporous and Mesoporous Materials,* vol. 204, pp. 156-162, 2015.

[11] L.-L. Lou, S. Jiang, K. Yu, Z. Gu, R. Ji, Y. Dong, *et al.*, "Mesoporous silicas functionalized with aminopropyl via co-condensation: Effective supports for

chiral Mn (III) salen complex," *Microporous and Mesoporous Materials,* vol. 142, pp. 214-220, 2011.

[12] R. Serna-Guerrero and A. Sayari, "Applications of pore-expanded mesoporous silica. 7. Adsorption of volatile organic compounds," *Environmental science & technology,* vol. 41, pp. 4761-4766, 2007.

[13] S. N. A. Rahman, "Preparation and characterization of tertiary amine functionalized MCM-41 for removal of nitrate from aqueous solution," Chemical Engineering, Universiti Teknologi Petronas, 2014.

[14] J. Virkutyte, E. Rokhina, and V. Jegatheesan, "Optimisation of electro-Fenton denitrification of a model wastewater using a response surface methodology," *Bioresource technology,* vol. 101, pp. 1440-1446, 2010.

[15] J. Wu, D. Yu, H. Sun, Y. Zhang, W. Zhang, F. Meng, *et al.*, "Optimizing the extraction of anti-tumor alkaloids from the stem of Berberis amurensis by response surface methodology," *Industrial Crops and Products*, vol. 69, pp. 68-75, 2015.

[16] M. A. Bezerra, R. E. Santelli, E. P. Oliveira, L. S. Villar, and L. A. Escaleira, "Response surface methodology (RSM) as a tool for optimization in analytical chemistry," *Talanta*, vol. 76, pp. 965-977, 2008.

[17] H. A. Hasan, S. R. S. Abdullah, S. K. Kamarudin, and N. T. Kofli, "Response surface methodology for optimization of simultaneous COD, NH4+–N and Mn2+ removal from drinking water by biological aerated filter," *Desalination*, vol. 275, pp. 50-61, 7/15/ 2011.

[18] L. Ma, Y. Han, K. Sun, J. Lu, and J. Ding, "Optimization of acidified oil esterification catalyzed by sulfonated cation exchange resin using response surface methodology," *Energy Conversion and Management*, vol. 98, pp. 46-53, 2015.

[19] M.-J. Chen, K.-N. Chen, and C.-W. Lin, "Optimization on response surface models for the optimal manufacturing conditions of dairy tofu," *Journal of Food Engineering*, vol. 68, pp. 471-480, 2005.

[20] L. Haller, P. McCarthy, T. O'Brien, J. Riehle, and T. Stuhldreher. *Nitrate Pollution of Groundwater*. Available: http://www.reopure.com/nitratinfo.html

[21] L. Niedziocha. (2013, August). *How Nitrates & Nitrites Affect Our Bodies*. Available: http://www.livestrong.com/article/509298-how-nitrates-nitrites-affect-our-bodies/

[22] J. R. Self and R. M. Waskom. (2014, August). *Nitrates in Drinking Water*. Available: http://www.ext.colostate.edu/pubs/crops/00517.html

[23] K. Farrell-Poe, L. Jones-McLean, and S. McLean, "Nitrate in Private Water Wells," 2010.

[24] H. J. Hannan, *Technician's Formulation Handbook for Industrial and Household Cleaning Products*: Lulu. com, 2007.

[25] M. K. Seliem, S. Komarneni, T. Byrne, F. Cannon, M. Shahien, A. Khalil, *et al.*, "Removal of nitrate by synthetic organosilicas and organoclay: Kinetic and isotherm studies," *Separation and Purification Technology*, vol. 110, pp. 181-187, 2013.

[26] E. Moll and D. Media. *Fertilizers As Pollutants*. Available: http://homeguides.sfgate.com/fertilizers-pollutants-78452.html

[27] A. Bhatnagar, E. Kumar, and M. Sillanp ää, "Nitrate removal from water by nano-alumina: Characterization and sorption studies," *Chemical Engineering Journal*, vol. 163, pp. 317-323, 2010.

[28] S. Holbrook. (2012, March). *Farming Communities Facing Crisis Over Nitrate Pollution, Study Says*. Available: http://thefern.org/2012/03/farming-communities-facing-crisis-over-nitrate-pollution-study-says/

[29] U. S. E. P. A. U. EPA). (2014). *Basic Information about Nitrate in Drinking Water* Available: http://water.epa.gov/drink/contaminants/basicinformation/nitrate.cfm

[30] B.-U. Bae, Y.-H. Jung, W.-W. Han, and H.-S. Shin, "Improved brine recycling during nitrate removal using ion exchange," *Water Research*, vol. 36, pp. 3330-3340, 2002.

[31] M. Soares, "Biological denitrification of groundwater," in *Environmental Challenges*, ed: Springer, 2000, pp. 183-193.

[32] G. Moussavi, S. J. Jafari, and K. Yaghmaeian, "Enhanced biological denitrification in the cyclic rotating bed reactor with catechol as carbon source," *Bioresource technology*, vol. 189, pp. 266-272, 2015.

[33] M. Kumar and S. Chakraborty, "Chemical denitrification of water by zero-valent magnesium powder," *Journal of hazardous materials,* vol. 135, pp. 112-121, 2006.

[34] S. Samatya, N. Kabay, Ü. Yüksel, M. Arda, and M. Yüksel, "Removal of nitrate from aqueous solution by nitrate selective ion exchange resins," *Reactive and Functional Polymers,* vol. 66, pp. 1206-1214, 2006.

[35] B. Dvorak and S. Skipton, "G08-1490 Drinking Water Treatment: Reverse Osmosis," 2008.

[36] D. Li and H. Wang, "Recent developments in reverse osmosis desalination membranes," *Journal of Materials Chemistry,* vol. 20, pp. 4551-4566, 2010.

[37] I. Petrinic, J. Korenak, D. Povodnik, and C. Hélix-Nielsen, "A feasibility study of ultrafiltration/reverse osmosis (UF/RO)-based wastewater treatment and reuse in the metal finishing industry," *Journal of Cleaner Production,* 2015.

[38] R. Saad, K. Belkacemi, and S. Hamoudi, "Adsorption of phosphate and nitrate anions on ammonium-functionalized MCM-48: Effects of experimental conditions," *Journal of colloid and interface science,* vol. 311, pp. 375-381, 2007.

[39] A. Ariapad, M. Zanjanchi, and M. Arvand, "Efficient removal of anionic surfactant using partial template-containing MCM-41," *Desalination,* vol. 284, pp. 142-149, 2012.

[40] A. Barrabino, "Synthesis of mesoporous silica particles with control of both pore diameter and particle size," 2011.

[41] W. L. Boncher, T. C. Lin, N. L. Cordes, and M. P. Hehlen, "Sequestration of cerium (III) bromide into mesoporous silica," *Microporous and Mesoporous Materials,* vol. 211, pp. 158-161, 2015.

[42] J. R. Deka, D. Saikia, Y.-S. Lai, C.-H. Tsai, W.-C. Chang, and H.-M. Kao, "Roles of nanostructures and carboxylic acid functionalization of ordered cubic mesoporous silicas in lysozyme immobilization," *Microporous and Mesoporous Materials,* vol. 213, pp. 150-160, 2015.

[43] F. Hoffmann, M. Cornelius, J. Morell, and M. Fröba, "Silica‐based mesoporous organic–inorganic hybrid materials," *Angewandte Chemie International Edition,* vol. 45, pp. 3216-3251, 2006.

[44] R. Richards, *Surface and nanomolecular catalysis*: CRC Press, 2006.

[45] V. K. Khanna, *Nanosensors: physical, chemical, and biological*: CRC Press, 2011.

[46] J. Y. Yang, J. Yang, Y. Zhou, W. G. Lin, H. J. Wang, and J. H. Zhu, "Effective nitrosamines trap derived from the in situ carbonized mesoporous silica MCM-41," *Journal of hazardous materials,* vol. 176, pp. 602-608, 2010.

[47] Y. Zhu, J. Zhou, J. Hu, and H. Liu, "The effect of grafted amine group on the adsorption of CO 2 in MCM-41: A molecular simulation," *Catalysis Today,* vol. 194, pp. 53-59, 2012.

[48] M. Vasudevan, P. L. Sakaria, A. S. Bhatt, H. M. Mody, and H. C. Bajaj, "Effect of Concentration of Aminopropyl Groups on the Surface of MCM-41 on Adsorption of Cu2+," *Industrial & Engineering Chemistry Research,* vol. 50, pp. 11432-11439, 2011.

[49] E. A. Prasetyanto and S.-E. Park, "Synthesis of short-channeled amino-functionalized SBA-15 and its beneficial applications in base-catalyzed reactions," *Applied Catalysis A: General,* vol. 350, pp. 244-251, 2008.

[50] J. M. Kokosa, A. Przyjazny, and M. Jeannot, *Solvent microextraction: theory and practice*: John Wiley & Sons, 2009.

[51] S. Sharma, A. Malik, and S. Satya, "Application of response surface methodology (RSM) for optimization of nutrient supplementation for Cr (VI) removal by Aspergillus lentulus AML05," *Journal of Hazardous Materials,* vol. 164, pp. 1198-1204, 2009.

[52] M. Aghaii, M. Pakizeh, and A. Ahmadpour, "Synthesis and characterization of modified UZM-5 as adsorbent for nitrate removal from aqueous solution," *Separation and Purification Technology,* vol. 113, pp. 24-32, 2013.

[53] M. Islam and R. Patel, "Physicochemical characterization and adsorption behavior of Ca/Al chloride hydrotalcite-like compound towards removal of nitrate," *Journal of hazardous materials,* vol. 190, pp. 659-668, 2011.

[54] M. Li, C. Feng, Z. Zhang, R. Chen, Q. Xue, C. Gao, *et al.*, "Optimization of process parameters for electrochemical nitrate removal using Box–Behnken design," *Electrochimica Acta,* vol. 56, pp. 265-270, 2010.

[55] L. Bois, A. Bonhommé, A. Ribes, B. Pais, G. Raffin, and F. Tessier, "Functionalized silica for heavy metal ions adsorption," *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* vol. 221, pp. 221-230, 2003.

[56] R. Buxton, "Design Expert 7: Introduction," ed, 2007.

[57] S. Huh, J. W. Wiench, J.-C. Yoo, M. Pruski, and V. S.-Y. Lin, "Organic functionalization and morphology control of mesoporous silicas via a co-condensation synthesis method," *Chemistry of materials,* vol. 15, pp. 4247-4256, 2003.

[58] J. Goldstein, *Practical scanning electron microscopy: electron and ion microprobe analysis*: Springer Science & Business Media, 2012.

[59] S. Jain, A. Bansiwal, R. B. Biniwale, S. Milmille, S. Das, S. Tiwari, *et al.*, "Enhancing adsorption of nitrate using metal impregnated alumina," *Journal of Environmental Chemical Engineering,* vol. 3, pp. 2342-2349, 2015.

[60] K. Parida and D. Rath, "Amine functionalized MCM-41: An active and reusable catalyst for Knoevenagel condensation reaction," *Journal of Molecular Catalysis A: Chemical,* vol. 310, pp. 93-100, 2009.

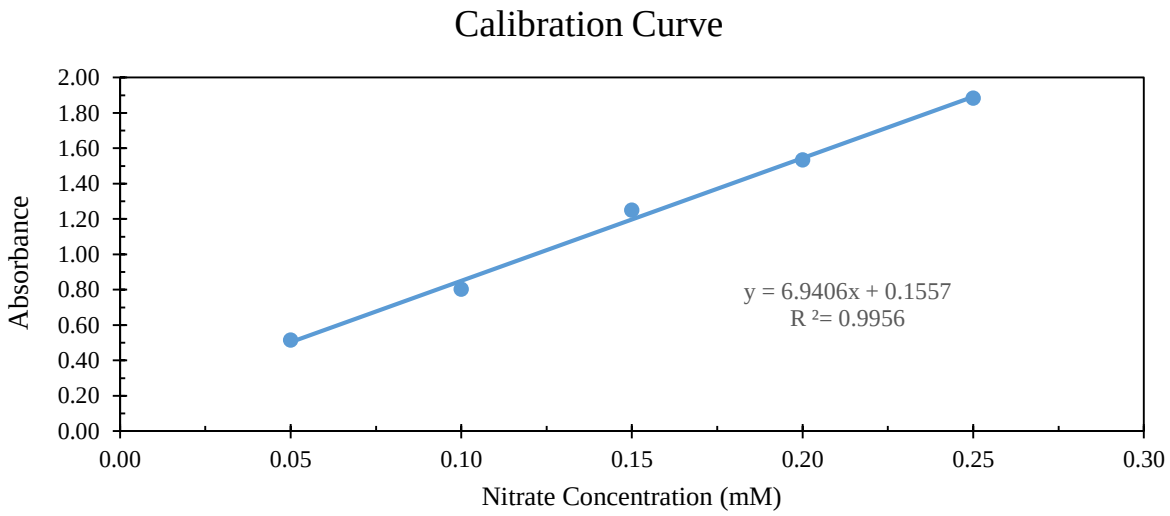
[61] X. Dai, F. Qiu, X. Zhou, Y. Long, W. Li, and Y. Tu, "Amino-functionalized MCM-41 for the simultaneous electrochemical determination of trace lead and cadmium," *Electrochimica Acta,* vol. 144, pp. 161-167, 2014.

[62] D. B. Nale, S. Rana, K. Parida, and B. M. Bhanage, "Amine functionalized MCM-41 as a green, efficient, and heterogeneous catalyst for the regioselective synthesis of 5-aryl-2-oxazolidinones, from CO 2 and aziridines," *Applied Catalysis A: General,* vol. 469, pp. 340-349, 2014.

[63] V. C. Srivastava, M. M. Swamy, I. D. Mall, B. Prasad, and I. M. Mishra, "Adsorptive removal of phenol by bagasse fly ash and activated carbon: equilibrium, kinetics and thermodynamics," *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* vol. 272, pp. 89-104, 2006.

APPENDICES

1) Nitrate Adsorption Study



$y = mx + C$

$Absorbance = 6.9406 * Final\ nitrate\ concentration + 0.1557$

- For experiment run 1:

$$Final\ nitrate\ concentration\ (mM) = \frac{0.7089 - 0.1557}{6.9406} = 0.07970$$

$$Percentage\ of\ Nitrate\ Removal\ (\%)$$

$$= \frac{Initial\ nitrate\ concentration - Final\ nitrate\ concentration}{Initial\ nitrate\ concentration}\ x\ 100\%$$

$$= \frac{0.15 - 0.07970}{0.15}\ x\ 100\%$$

$$= 46.86\%$$

Result for all the 19 experiments:

Exp run	A: Initital Nitrate Concentration (mM)	B: Weight of Adsorbents (g)	C: Contact Time (h)	Absorbance	Final Nitrate Concentration (mM)	Percentage of Nitrate Removal (%)
1	0.15	0.275	24.00	0.7089	0.07970	46.86
2	0.15	0.275	12.50	0.7075	0.07950	47.00
3	0.15	0.050	12.50	0.9235	0.11062	26.25
4	0.05	0.275	12.50	0.4701	0.04530	9.40
5	0.05	0.500	1.00	0.4350	0.04024	19.52
6	0.05	0.050	24.00	0.4308	0.03964	20.73
7	0.25	0.050	24.00	1.1278	0.14006	43.98
8	0.25	0.500	24.00	0.6885	0.07677	69.29
9	0.25	0.050	1.00	1.1088	0.13732	45.07
10	0.25	0.500	1.00	0.6718	0.07436	70.26
11	0.15	0.500	12.50	0.7032	0.07888	47.41
12	0.15	0.275	12.50	0.7089	0.07970	46.86
13	0.05	0.050	1.00	0.4883	0.04792	4.16
14	0.15	0.275	12.50	0.7526	0.08600	42.67
15	0.15	0.275	1.00	0.7126	0.08024	46.51
16	0.15	0.275	12.50	0.7486	0.08542	43.05
17	0.05	0.500	24.00	0.4315	0.03974	20.53
18	0.15	0.275	12.50	0.6991	0.07829	47.80
19	0.25	0.275	12.50	0.7511	0.08579	65.69

2) Isotherms Study

Note: Final nitrate concentration, Ce (mM) is predicted through the model from DoE software.

Langmuir Isotherm

$$\frac{\mathbf{1}}{\boldsymbol{q_e}} = \frac{\mathbf{1}}{\boldsymbol{q_m K_L}} \frac{\mathbf{1}}{\boldsymbol{C_e}} + \frac{\mathbf{1}}{\boldsymbol{q_m}}$$

- For 0.05 mM:

$$C_i = \frac{0.05\ x\ 10^{-3}\ mol}{L} x \frac{62000\ mg}{mol} = 3.1\ mg/L$$

$$C_e = \frac{0.048\ x\ 10^{-3}\ mol}{L} x \frac{62000\ mg}{mol} = 2.976\ mg/L$$

$$q_e = (C_i - C_e)\ x\ \frac{V}{m}$$

$$q_e = \frac{(3.1 - 2.976)\ mg}{L}\ x\ \frac{0.025\ L}{0.05\ g} = 0.062\ mg/g$$

(i) For 0.05 g of adsorbent and contact time of 1 h:

Initial nitrate concentration, C_i (mM)	**Initial nitrate concentration, C_i (mg/L)**	**Final nitrate concentration, C_e (mM)**	**Final nitrate concentration, C_e (mg/L)**	**Adsorption capacity, q_e (mg/g)**	**$1/C_e$**	**$1/q_e$**
0.05	3.1	0.048	2.976	0.062	0.33602	16.12903
0.10	6.2	0.082	5.084	0.558	0.19670	1.79212
0.15	9.3	0.106	6.572	1.364	0.15216	0.73314
0.20	12.4	0.124	7.688	2.356	0.13007	0.42445
0.25	15.5	0.138	8.556	3.472	0.11688	0.28802

(ii) For 0.275 g of adsorbent and contact time of 1 h:

Initial nitrate concentration, C_i (mM)	Initial nitrate concentration, C_i (mg/L)	Final nitrate concentration, C_e (mM)	Final nitrate concentration, C_e (mg/L)	Adsorption capacity, q_e (mg/g)	$1/C_e$	$1/q_e$
0.05	3.1	0.045	2.790	0.028	0.35842	35.48387
0.10	6.2	0.069	4.278	0.175	0.23375	5.72320
0.15	9.3	0.078	4.836	0.406	0.20678	2.46416
0.20	12.4	0.077	4.774	0.693	0.20947	1.44243
0.25	15.5	0.072	4.464	1.003	0.22401	0.99674

(iii) For 0.50 g of adsorbent and contact time of 1 h:

Initial nitrate concentration, C_i (mM)	Initial nitrate concentration, C_i (mg/L)	Final nitrate concentration, C_e (mM)	Final nitrate concentration, C_e (mg/L)	Adsorption capacity, q_e (mg/g)	$1/C_e$	$1/q_e$
0.05	3.1	0.04	2.48	0.0310	0.40323	32.25806
0.10	6.2	0.061	3.782	0.1209	0.26441	8.27130
0.15	9.3	0.069	4.278	0.2511	0.23375	3.98248
0.20	12.4	0.071	4.402	0.3999	0.22717	2.50063
0.25	15.5	0.075	4.65	0.5425	0.21505	1.84332

Freundlich Isotherm

$$log\ q_e = logK_F + \frac{1}{n} logC_e$$

(i) For 0.05 g of adsorbent and contact time of 1 h:

Initial nitrate concentration, C_i (mM)	Initial nitrate concentration, C_i (mg/L)	Final nitrate concentration, C_e (mM)	Final nitrate concentration, C_e (mg/L)	Adsorption capacity, q_e (mg/g)	Log C_e	Log q_e
0.05	3.1	0.048	2.976	0.062	0.47363	-1.20761
0.10	6.2	0.082	5.084	0.558	0.70621	-0.25337
0.15	9.3	0.106	6.572	1.364	0.81770	0.13481
0.20	12.4	0.124	7.688	2.356	0.88581	0.37218
0.25	15.5	0.138	8.556	3.472	0.93227	0.54058

(ii) For 0.275 g of adsorbent and contact time of 1 h:

Initial nitrate concentration, C_i (mM)	**Initial nitrate concentration, C_i (mg/L)**	**Final nitrate concentration, C_e (mM)**	**Final nitrate concentration, C_e (mg/L)**	**Adsorption capacity, q_e (mg/g)**	**Log C_e**	**Log q_e**
0.05	3.1	0.048	2.976	0.062	0.44560	-1.55003
0.10	6.2	0.082	5.084	0.558	0.63124	-0.75764
0.15	9.3	0.106	6.572	1.364	0.68449	-0.39167
0.20	12.4	0.124	7.688	2.356	0.67888	-0.15910
0.25	15.5	0.138	8.556	3.472	0.64972	0.00142

(iii) For 0.50 g of adsorbent and contact time of 1 h:

Initial nitrate concentration, C_i (mM)	**Initial nitrate concentration, C_i (mg/L)**	**Final nitrate concentration, C_e (mM)**	**Final nitrate concentration, C_e (mg/L)**	**Adsorption capacity, q_e (mg/g)**	**Log C_e**	**Log q_e**
0.05	3.1	0.048	2.976	0.062	0.39445	-1.50864
0.10	6.2	0.082	5.084	0.558	0.57772	-0.91757
0.15	9.3	0.106	6.572	1.364	0.63124	-0.60015
0.20	12.4	0.124	7.688	2.356	0.64365	-0.39805
0.25	15.5	0.138	8.556	3.472	0.66745	-0.26560